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The effect of time, temperature and particle size on the release of bases from some common soil-forming minerals of different crystal structure

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THE EFFECT OF TIME, TEMPERATURE AND PARTICLE
SIZE ON THE RELEASE OF BASES FROM SOME COMMON SOIL-
FORMING MINERALS OF DIFFERENT CRYSTAL STRUCTURE

by

John Edward McClelland

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

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I. INTRODUCTION

The capacity of soils for supplying nutrient elements to plants is of great importance to man. Although commercial fertilizers can be used to supplement nutrient deficiencies in soils, the visible supply of fertilizers is not large enough to continuously supply all of the nutrients for all of the plants grown. Fortunately, most soils contain a rather wide assortment of minerals, which upon weathering, make their constituents available to plants. If the soil can supply nutrients to plants in the correct proportions and quantities, and at the right times, and if other factors are favourable, plants will flourish. It is one of the aims of those interested in the study of soils to be able to evaluate the nutrient supplying potential of soils so that deficiencies can be foreseen and corrected. For this reason the release of bases from soils, particularly potassium, has been dealt with by numerous investigators.

Recently more attention has been directed toward the mineralogical content of soils. Improved methods have been devised to identify and quantitatively determine the mineral constituents. Many of the studies of the primary minerals in soils have dealt with the heavy mineral group, some of the more resistant of these

being used as markers in the study of soil profile development. While the rate with which the non-exchangeable ions are released from the minerals contained in the soil to the exchangeable and/or plant available forms has been determined for many soils, little quantitative information is available as to the role played by the individual minerals. The importance of particle size and base release from minerals has been recognized by many authors, but data on the subject are scanty. It has been known for some time that grinding certain minerals in water causes an immediate and marked increase in the pH of the mixture. However, the rate at which this reaction continues is still in doubt.

Geologists have conducted numerous investigations concerning the stability relationships of minerals. Much of the work has been directed toward the hydrothermal synthesis and alteration of minerals, the process being accelerated by the use of high pressures. Stability relationships have usually been estimated from optical observations. Mineralogists, aided by X-ray diffraction studies, have established the crystal form of most minerals and have improved the methods for their identification. Thus knowledge of the minerals found in soils is increasing at a rapid pace.

Two important criteria used in the classification of soils are soil texture and geological origin of the deposits from which soils are derived. In Iowa no mineralogical data is available showing the distribution of minerals in soil profiles. Data obtained by the Iowa Geological survey (35) indicate that there is little difference in the kind of minerals present in the various Pleistocene deposits encountered in Iowa. For instance, if the minerals present in the Clarion and Marshall soils are similar, then the much higher exchangeable potassium in the Marshall series (29) (48) must be explained on some other basis. Mechanical analyses of these two soils show that the Clarion soil contains between 40 and 50 percent sand (48) whereas the Marshall soil contains very little, probably less than 10 percent sand. Thus the finer subdivision of the minerals present in the Marshall soil may be related to its high rate of release of potassium. However, the extent to which particle size and base release are related, has not been determined.

In order to interpret mineralogical analyses of soils from a pedological viewpoint, information is necessary both as to the rate at which the various minerals decompose and the effect of subdivision on

this rate. Certain minerals, in the coarse sizes at least, may release ions too slowly to contribute materially to plant needs. If this is the case, a study of the decomposition rate of various minerals may show which minerals should be most carefully observed.

The object of this study is to determine the rate with which minerals release non-exchangeable bases to the exchangeable form and to determine the effect that particle size, temperature and degree of base saturation have on this reaction. This information should be of value in the interpretation of mineralogical and mechanical analyses of soils from both the fertility and profile development standpoints. While a solution to this entire problem is beyond the scope of this investigation, it is hoped that this study may form a foundation for further research.

II. REVIEW OF LITERATURE

A. Classification and Structure of Silicate Minerals

The silicate minerals form the largest proportion of the constituents of the earth's crust, and as such they have received a good deal of attention. Although the crystal structures of all of these minerals have not been completely determined, the majority of the common silicate minerals have been intensively studied. Bragg (7) has summarized and supplemented the available information on crystal structure of silicate minerals up to 1937. Since that time the micas have been further investigated by Hendricks and Jefferson (26), Volk (57), and others. The clay minerals have been the object of numerous investigations and considerable information is now available concerning their properties and structure (21) (36). Recently, Barshad (3) has identified a vermiculite-like mineral in California soils and has made a detailed study of the weathering characteristics of this mineral.

A classification of minerals has been outlined by Dana (13) based on chemical composition and optical and physical properties. A brief outline of this classification is presented in Table 1, including the common minerals of each division or group. Also included is a brief description of their crystal structure as outlined

by Bragg (7). Information concerning the clay mineral group was obtained from Grim (21) and the kaolin division given by Dana (13) was enlarged to include these minerals. Data on vermiculite was obtained from Barshad (3).

Table 1

TYPES OF SILICATE MINERALS

I Anhydrous Silicates

Orthosilicates (R_2SiO_4), e.g. garnet, olivine, zircon, epidote. The crystal lattice consists of silica tetrahedra linked together through divalent bases, mainly Mn, Fe and Mg.

Metasilicates ($RSiO_3$), e.g. pyroxene and amphibole groups. The pyroxenes consist of silica tetrahedra linked in single chains, each silicon atom being linked to the succeeding one through oxygen bonds. The remaining oxygen bonds of the silica tetrahedra link the chains together through bases, each of which is surrounded by six oxygen atoms. The amphiboles are quite similar except that two silica chains are linked together directly and the pairs of silica chains are linked through bases as for the pyroxenes.

Disilicates (RSi_2O_5) and Polysilicates ($R_2Si_2O_7$), e.g. feldspars. The feldspars consist of frameworks of linked silica and alumina tetrahedra with the cations K, Mg, Ca, or Ba situated in the interstices of the negatively charged framework of tetrahedra.

Subsilicates, e.g. tourmaline and staurolite. These are basic salts mainly of A and B. The structures vary.

Table 1 (continued)

II Hydrous Silicates

Zeolites. The structure of this group of minerals is similar to the feldspars except the arrangement of atoms is less compact and they contain loosely held water.

Mica Division, e.g. micas, chlorites and vermiculite. These structures are based on a hexagonal network of linked silicon-oxygen tetrahedra. In the case of the micas two such layers are combined by octahedral co-ordination (about Al, Mg, Fe, etc.) of their unshared oxygen and hydroxyl ions. K atoms at the centres of the O hexagons of the silica layers link successive sheets, each K atom neighboring 12 O atoms. The Chlorites differ in that they contain alterhate mica-like and brucite-like layers. Barshad (3) indicates the structure of vermiculite closely resembles a Mg mica wherein K is replaced by Mg.

Serpentine and Talc Division. Serpentine may be an end member of the chlorite group, whereas Talc more closely resembles the micas. In talc the double sheets are neutral due to the replacement of the Al in the mica structure by Si.

Clay Mineral Division.

1. Illite group. Structure similar to muscovite.
2. Montmorillonite group, e.g. montmorillonite, beidellite and nontronite. These minerals are similar in structure to muscovite but have an expanding lattice due to the absence of bonds between adjacent silica sheets.
3. Kaolinite group, e.g. kaolinite, dickite and nacrite. Similar in structure to the montmorillonite group except they contain but one silica sheet, the Al sheet being balanced by OH ions.

B. Pedologic and Related Research

The weathering of rocks and minerals has been studied by geologists and pedologists. The geologist is interested in weathering as a measure of the geological age of deposits and as an aid in the recognition of the source of secondary deposits. The pedologist is interested in weathering as it affects soil-plant relationships, the physical properties of soils and soil profile development. Although the aims of these two groups are toward different ends often their work is complementary.

Van Hise (56) in 1904 made a thorough review of the knowledge of metamorphism to that time. Referring to muscovite he said (56, p. 337):

One of the most frequent alterations is that of hydration, a part of the potassium being replaced by hydrogen; or at the same time it may take up other bases and thus the mineral may pass into vermiculite, a somewhat indefinite compound to which no formula can be assigned.

Much of the literature dealing with the release of bases from minerals prior to 1905 has been summarized by Cameron and Bell (10). In general it was found that aside from the initial release caused by grinding, the silicate minerals were too stable to be used as fertilizers without additional treatment.

Cameron and Bell (10) were probably the earliest workers in soils to use electrodialysis as a means of

studying mineral breakdown. They dialyzed a few minerals for 2 weeks with a potential of 40 volts and for 8 more weeks at 80 volts. Their data are contained in table 2.

Table 2

Electrodialysis Data of Cameron and Bell (10, p.28)

Mineral	Base Determined	Total Amount of base present mg	mg base release in		
			First 2 weeks	Next 2 weeks	Last 6 weeks
Orthoclase	K ₂ O	129	.6	.5	.9
Muscovite	K ₂ O	96	1.1	1.3	2.3
Hornblende	MgO	281	4.9	2.9	3.8
Serpentine	MgO	395	8.2	5.7	5.5

They also studied the effect of dilute solutions, about 1 percent concentration of potassium chloride and sodium nitrate, on the release of bases from minerals using water as a check. The ratio of mineral to water was 1:100. The mixtures were kept in sealed paraffin cylinders for 14 months. In the cases of orthoclase and muscovite they found that more acid was required to neutralize the bases released from the water-mineral checks than from either salt solution. The sodium nitrate solutions required the least acid. With albite the difference between the check and salt treatments was even more pronounced. In the case of hornblende the sodium chloride solution required most acid for neutral-

ization followed by potassium chloride, sodium nitrate and water in that order. No explanation for these differences was offered. The hornblende mixtures were shaken.

Blanck (4) as reported by Denison, Fry and Gile (14) came to the following conclusions concerning muscovite and biotite:

1. Muscovite as well as biotite releases potash to plants, and both are as well adapted for supplying potash as potash feldspar.
2. The release of potash to plants by muscovite is in opposition to the prevailing opinion as to the capacity of this mineral to weather, pointing, as it does, to an actual weathering. This appears to consist in removal of potash but with preservation of the external physical properties of the mineral.

DeTurk (15) conducted experiments using potassium bearing minerals as fertilizers and concluded that their solubility in water was very slight. However, ammonium chloride and decomposing alfalfa caused some increase in the potassium released. It was assumed that ammonia was produced as a decomposition product from the alfalfa and so these treatments were related.

Bouyoucos (5) ground numerous rocks and minerals and found that while the first water extraction produced considerable salts, subsequent extractions at intervals up to 100 days contained but few. Incubation at 53

degrees C. for 95 days caused big increases in salts in solution except for shale and kaolinite. Steam pressure of 26 pounds for 8 hours was also found to be very effective for releasing salts. He did not find that other salt solutions used as weathering agents had any appreciable effect. The salts released were measured by a freezing point depression method. Bouyoucos believed that solution was the main factor in the production of salts at ordinary temperatures, whereas hydrolysis became more important at higher temperatures.

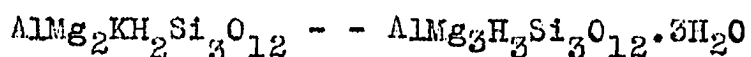
Vandecaveye (55) found that manure extract with or without dilute mineral acids (.01 to .02 N.) caused a marked increase in the release of potassium from orthoclase and alunite. Sterilization, very dilute acids (less than .02 N.), calcium carbonate and calcium sulfate did not increase the quantity of water soluble potassium that could be extracted from these minerals.

Clarke (11, p. 399) in an extensive treatment of the data available on geochemistry states:

Muscovite, under ordinary conditions, is one of the least alterable of minerals. The feldspar of a granite may be completely kaolinized, while the embedded plates of mica retain their brilliancy almost unchanged.

He further states (11, p. 399):

Unlike muscovite, biotite and phlogopite alter easily, and pass into a series of apparently indefinite substances known as "vermiculites". The change, however, is very simple, and consists merely in the replacement of the alkaline metals by hydrogen, with assumption of additional, loosely combined water. From the typical ferromagnesium micas the following derivatives are thus formed:



Winchell (61) studied the mica group in some detail and postulated that atomic volumes are the primary consideration in the replacement of ions in the crystal lattice. Only those ions with similar atomic volumes are interchangeable, e.g. oxygen, hydroxyl, chlorine and fluorine ions in the micas.

Breazeale and Magistad (8) in a study of orthoclase found that the solubility varied with, (1) the origin of the sample, (2) particle size and, (3) ratio of mineral to water in the incubation mixture. They found that the treatment of orthoclase with a basic solution caused an increase in its exchange capacity whereas an acid treatment had the opposite effect. Heat caused the destruction of these exchange properties but this could be counter-acted by treatment with an alkali solution. They thought that potassium was hydrolyzed from orthoclase in a manner similar to the hydrolysis of zeolites and that it was not a strict solubility relationship. They

proposed that the hydrolysis of orthoclase resulted in the formation of potassium hydroxide, which in turn combined with aluminum oxide to form potassium aluminate. Their samples may have contained some microcline but they did not distinguish between orthoclase and microcline.

Denison, Fry and Gile (14) studied the alteration of muscovite and biotite in eleven soil profiles obtained from the region of the Piedmont Plateau. They found that average soil muscovite differed from average fresh muscovite in being lower in potassium and higher in water. Average soil biotite contained more alumina, silica and water and less magnesium, potassium and iron than average fresh biotite. The smaller mica fragments were altered more than the larger ones. They did not think that alteration of the micas is accomplished simply by the replacement of potassium by hydrogen. They presented evidence to show that alteration proceeds in such a manner that ultimately kaolinite is formed.

The data of Denison and associates (14) indicate that the composition of the mica is relatively constant above the lower C horizon of the soil. However, the quantity of mica present diminishes with depth and a corresponding increase in the kaolinite content occurs.

Judging from the relative abundance of minerals throughout the profile they believe that the loss of mica has been proportionately greater than the loss of other minerals. Whereas the percentage of mica decreases as the surface is approached the greatest decrease occurs in the transition from the C to B horizons. This difference is more pronounced in the soils showing greatest profile development. They were of the opinion that some secondary muscovite may be formed in the B - C transition layer accounting for this sudden increase. This may also explain that in a few profiles the ratio increases in the B - C transition layer although in most profiles the ratio of muscovite to biotite is relatively constant.

In most of the profiles studied by Denison and co-workers (14) the potash content of biotite was about 4 percent, whereas it varied from 1 to 8 percent for muscovite. The presence of secondary muscovite in variable quantities in different profiles could be responsible for this wide range in potash content. They conclude that the rates at which muscovite and biotite decompose in the soil are very similar.

Stevens (51) ground several alumino-silicates under water in a nitrogen atmosphere. He found that these

minerals hydrolyzed to give characteristic and reproducible pH values. He suggested that pH could be used as a measure of the weathering qualities of minerals.

Volk (58) studied the fixation of potassium in a heavily fertilized soil for which only half of the potassium added over a period of 50 years could be accounted for by crop removal or as being present in the available form. He postulated that muscovite was formed in the colloidal fraction.

Tamm (54) carried on experiments with potassium feldspar, muscovite and other minerals and observed the effect of grinding in benzene and in water. Judging from the similarity of the behavior of muscovite and feldspar he thought that the crystal lattice of the feldspar may have been rearranged in water to that of muscovite.

Alexander and Byers (1) ball milled and electro-dialyzed anorthite. Grinding increased both the moisture content of the sample at 110 degrees C. and the ignition loss. This evidence, together with the X-ray pattern, indicated to them that halloysite was a product formed although some of the anorthite X-ray pattern was still evident. By electro-dialyzing the ground mineral, followed by drying, regrinding and electro-dialyzing at intervals the calcium oxide content of anorthite was reduced from

17 to 2 percent and the water content increased from 0 to 18.3 percent.

Kelley and Jenny (37) studied the relation of crystal structure and base exchange of pure minerals and its bearing on base exchange in soils. Orthoclase, four plagioclase feldspars, biotite and muscovite all showed increases in base exchange capacities with grinding. For biotite and muscovite the increase was equal to the potassium released. Whereas biotite released about the same number of ions of magnesium as of potassium, the magnesium released did not increase the exchange capacity. Chlorite and prochlorite showed some increase in exchange properties on grinding whereas talc, bauxite and quartz did not, although talc released a considerable amount of magnesium. The exchange capacity of both kaolinite and pyrophyllite increased many times, whereas that of bentonite was only doubled. The colloids from the Cecil and Yolo soil series increased in exchange capacities on grinding from 17 and 67 milliequivalents per hundred grams to 151 and 166, respectively.

Buehrer and Williams (9) studied the effect of dilution on the pH of various soil minerals. Their research indicated that in the case of the alumino-silicate minerals the equilibrium pH of the resulting mixtures decreased toward a constant minimum value with dilution. Repeated washing of the minerals also caused a marked decrease in

the pH of the successive washings. Bentonite was the only exception in both instances. They considered that their data may be indicative of continuous break-down of these silicate minerals.

Jeffries and White (33, 34) investigated the mineralogical composition of a Hagerstown profile. The feldspars constituted from 7 to 46 percent of the total sands. The parent dolomitic rock contained a small amount of weathered orthoclase and considerable microcline. The orthoclase disappeared within twenty inches of the parent rock. A material similar to a plagioclase feldspar coated some of the microcline particles and as the surface of the profile was approached sodium apparently replaced calcium in this material. The sand fraction contained 7.6 percent feldspars in the surface horizon and 36.5 percent feldspars in the lower B horizon.

Correns and Von Englehardt (12) quantitatively followed the decomposition of a pulverized potash feldspar (adularia). They leached the fractionated mineral with solutions at various hydrogen ion concentrations and found that 2 liters of these solutions with pH values of 3, 6.6 and 11 removed 18.2, 9.6 and 14.2 percent respectively of the original potash content. The less than 1 micron fraction released twice as much potash as the 3 to 10 micron fraction when

about 2 liters of solution were leached through them. Raising the temperature from 20 to 40 degrees centigrade more than doubled the amount of potash released from the less than 1 micron fraction. They proposed that the feldspars go into solution in ionic form. A thin hull of fairly constant thickness apparently is formed around the unweathered portion of the particles. The composition of this hull depends on the pH of the solution. The ratio of silica to alumina in this residual layer was never observed to be less than 5. The diffusion of potassium ions into this residual layer was thought to be of the order of magnitude of diffusion in solid bodies.

Correns and Von Englehardt (12) found that reduction of particle size and elevation of temperature accelerated the decomposition rate of the mineral but did not seem to alter the composition of the residual layer. They calculated the volume of solution at various hydrogen ion concentrations that would be required to completely dissolve a given quantity of feldspar. They suggest that the regrowth of minerals may take place in very dilute ionic solutions and at ordinary temperatures in a manner similar to the formation of the residual layer.

Jackson and Truog (30) ground microcline, talc, quartz and several of the clay minerals to a very fine degree of subdivision. Practically all of the bases could then be

replaced by neutral, normal ammonium acetate solution and both silica and alumina became quite soluble in very dilute acids, dilute sodium carbonate solution and neutral salt solutions. Apparently prolonged grinding disrupted the more stable valence bond relationships in the silicates.

Graham (18, 19, 20) conducted a series of investigations of some of the primary minerals commonly found in soils. He (18) separated the silt fraction of several ground pure minerals, leached them with .001 N hydrochloric acid and incubated them in a 4 percent suspension of hydrogen saturated Putnam colloid. The pH of the suspension increased for all of the minerals studied except for quartz. Biotite, microcline and augite reached almost stable and similar pH values within 31 days. Anorthite increased the pH of the mixture much more than did the other minerals and had not reached a maximum pH in 107 days. Hornblende occupied an intermediate position. Hydrolysis of the minerals accounted for a very small portion of the bases released. In another experiment on the weathering of anorthite, Graham (19) noted several colloidal organic acids were almost as effective as hydrogen saturated bentonite in removing calcium. He (20) later proposed a fertility rating of soils based on the abundance of feldspars and certain heavy minerals in the sand and silt fractions.

Alexander, Hendricks and Faust (2) found that gibbsite is contained in the primary weathering products from aluminous hornblende, plagioclase feldspar, epidote and biotite. They postulated that resilication of gibbsite to form kaolinite can take place when aluminosilicate minerals weather. This resilication probably occurs within a few centimeters of the rock surface. Their observations are somewhat similar to those of Correns and Von Englehardt (12). Harrison (25), Hardy and Rodrigues (23,24) previously had reported the presence of gibbsite in the weathering products of several aluminosilicate minerals.

Humbert and Marshall (27) conducted a comprehensive mineralogical and chemical investigation of two residual soils developed from acid and basic igneous rocks in Missouri. They found that some of the more easily weathered minerals persist in the surface layers and suggest that it may be related to their original size. Considerable secondary quartz was present in the upper horizons of the residual diabase profile whereas little, if any, was present in the profile derived from granite. The principal clay mineral present in both profiles appeared to be beidellite and lesser amounts of micaceous minerals.

Humbert and Marshall (27) suggest that there are three chemical weathering forces, water, carbonic acid and oxygen,

which act simultaneously, the carbonic acid and oxygen being dissolved in the water. The structure of the mineral should determine the extent to which chemical weathering takes place, the ions in the less compact structures being more accessible to water. The calcium feldspars weather more rapidly than the potash feldspars possibly due to their higher unit charge. The replacement of metals by hydrogen or the oxidation of ferrous iron to the ferric state, accompanied by the addition of an hydroxyl ion, may cause the disruption of the crystal lattice in many cases. Although the pyroxenes and amphiboles have very dense structures they have numerous cracks along the cleavage planes which facilitate the penetration of water. Gibbsite did not appear to be formed in the diabase profile.

Reitemeier and co-workers (47) studied the release of non-exchangeable potassium by several methods. Correlation between the release of potassium by two years of continuous ladino clover growth, 30 days of electrodialysis, a modified Neubauer method procedure, and digestion in normal boiling nitric acid for 10 minutes, were highly significant. The relationship between the release of potassium by the clover and electrodialysis treatments was in the same order of magnitude and more precise.

C. Methods of Studying the Weathering of Minerals and Mineral Stability Relationships

Several methods have been employed in determining the rates with which minerals weather. Many geologists have investigated the alteration and synthesis of minerals at high temperatures and pressures usually in the presence of water, with varying degrees of success. Morey and Ingerson (43) have summarized much of the literature on this subject prior to 1937 and it will not be dealt with here.

Electrodialysis was one of the earliest quantitative measures used in the study of weathering. Cameron and Bell (10) had a simple electrodialysis cell made up of a glass container in which a smaller porous cup was placed. Another porous cup was placed inside the first porous cup to act as the anode chamber. The material to be dialyzed was placed in the central chamber and the cathode was located in the outer chamber. They electrodialyzed ground minerals using a potential of 40 and 80 volts and found that bases were removed from orthoclase, muscovite, hornblende and serpentine. The total amount of bases removed increased in the order the minerals are written but with time the rate of removal decreased.

Mattson (41) designed an electrodialysis cell divided into 3 compartments by two parchment membranes. Employing a potential of 220 volts in his electrodialysis apparatus he found that 42 hours were required to remove as many bases as could be removed by a normal ammonium acetate solution. The cations were removed in the following order: Ca, Na and K; Mg; Al, Mn and Fe. Mg behaved like Al and Fe and did not migrate to any appreciable extent until the pH of the central compartment of the electrodialysis cell was reduced by the migration of other strong bases. Humfeld and Alben (28) found that the potential employed during electrodialysis could be dropped to 50 to 55 volts with only a slight increase in the time of operation. The lower voltage resulted in a decreased heating effect.

Hall (22) developed a method of electrodialysis whereby the mixture to be dialyzed is placed between two platinum electrodes and continuously or intermittently leached. Alternating current with a frequency of between .02 and .5 cycles per second and a potential of 90 to 110 volts was found to be most satisfactory as this prevented the accumulation of the products. Acid treated quartz sand was used as a filler to improve the infiltration capacity of the mixture. This method provided useful information regarding the mechanism of clay movement in the

soil profile and may provide a means of studying clay formation.

Stevens (51, 52) suggested that the pH of ground silicate minerals could be used as a measure of their weathering qualities. The minerals were ground under water for 2 minutes in a nitrogen atmosphere and the pH of the mixture was determined. The results were quite reproducible but considerable variation was evident between different samples of the same mineral. Of the minerals observed muscovite, biotite and orthoclase showed the lowest pH values and hornblende, augite and pyroxene, the highest.

Steidtmann (50) compared the effect of weathering and hot solutions on the alteration of rocks and did not find much relationship between the two processes. Weathering removes constituents in decreasing amounts in the order listed: lime, magnesia, soda, potash, silica, iron and alumina. In very basic igneous rocks magnesia may be lost faster than lime. Leith and Mead (39) observed the same relationship but placed soda ahead of magnesia. They pointed out that magnesia and iron show large fluctuations in the amounts removed.

Goldich (17) proposed a mineral-stability series in weathering based on the changes in composition of partially weathered and unweathered rock as revealed by chemical

and mineralogical analyses. This series is presented in Table 3 (17, Table 18, p. 56).

Table 3

Goldich's Mineral Stability Series in Weathering

Olivine	Calcic plagioclase
Augite	Calcic-alkalic plagioclase
Hornblende	Alkali-calcic plagioclase
	Alkalicplagioclase
Biotite	Potash feldspar
	Muscovite
	Quartz

Goldich pointed out that his stability series is the exact reverse of Bowen's (6) reaction series. The reaction series of Bowen indicates the stability of minerals under the equilibrium conditions which prevailed when igneous rock-forming minerals were crystallized. Goldich states (17, p. 56):

Perhaps the differential between equilibrium conditions at the time of formation and those existing at the surface govern the order of stability.

Pettijohn (45) tabulated data concerning the persistence of heavy minerals in partially weathered deposits of various geologic ages and found complete agreement with Goldich's stability series. He proposed the addition of twenty heavy minerals to the series and lists their order of stability. Smithson (49) also compiled a more inclusive

stability series than the one proposed by Goldich which roughly agreed with Pettijohn's series.

Marshall and Jeffries (40) presented a detailed procedure suitable for mechanical and mineralogical analyses of soils. They included a section designed to help interpret the results obtained from these analyses.

Graham (19) suggested the use of hydrogen saturated colloid as a weathering agent for minerals. He estimated that it was about 100 times more effective than the hydrolytic action of water.

Jackson and associates (31) proposed a weathering sequence for minerals of clay size that are found in soils. Their series is in agreement with Goldich's stability series and that of Pettijohn except they extended it to cover the clay minerals and several other minerals found in soils. They suggested 13 weathering stages in their sequence, each stage being the resultant of intensity factors and capacity factors, and also characterized by the presence of certain minerals. They postulated that a distribution curve of the clay size minerals should reveal the stage of weathering of a sample.

Jeffries (32) has made a preliminary report on a method of recognizing the essential minerals in soils using an X-ray spectrometer. The X-ray diffraction pattern

of the sample under investigation is compared to standard patterns of the different minerals. He suggested that weathering processes in the soil may be studied by following the change in mineral distribution with decrease in particle size.

III. MATERIALS AND METHODS

A. Selection of Minerals

Kay and Graham (35) have summerized the mineralogical data available for the Pleistocene deposits of Iowa. These analyses indicate that the feldspars, amphiboles, pyroxenes and micas, are among the commoner primary silicate minerals encountered. In general the distribution of minerals within the different Pleistocene deposits of Iowa shows a marked similarity. Although local variations in mineral content are encountered within each major deposit, no consistent variation within any one deposit was observed. There is no data available showing the distribution of minerals in Iowa soils although the geological origin of the parent material is an important criteria in the establishment of soil series.

As the feldspars, amphiboles, pyroxenes and micas are known to be common constituents of the Pleistocene deposits in Iowa and many other localities, this study has mainly been limited to these minerals. A specimen of olivine was included as a representative of the orthosilicate group of minerals. As the potassium-bearing minerals are so important to soil fertility, the selection was preferentially weighted with these minerals. The pure mineral samples were obtained from Wards Natural Science Establishment of New York.

Table 4 contains a list of the minerals investigated showing their division in the classification scheme outlined in table 1, their theoretical composition, place of origin and specific gravity. Except for hornblende the composition and specific gravity data were obtained from Dana (13). The composition of hornblende was obtained from Bragg (7).

Table 4

Classification, Composition, Origin and Specific Gravity
of Minerals Investigated

Division in Classification	Mineral	Composition*	Place of Origin	Specific* Gravity
Orthosilicate	Olivine	$(\text{Mg,Fe})_2\text{SiO}_4$	Jackson County N.C.	3.3-3.6
Metasilicate	Augite	$\text{Ca Mg}(\text{SiO}_3)_2$ with $(\text{Mg,Fe})(\text{Al,Fe})_2\text{SiO}_6$	Hybla, Ontario	3.2-3.6
	Hornblende	$(\text{Ca,Na})_2(\text{Na,K})_{0-1}\text{Mg}_1 -$ $(\text{Mg,Al})_4(\text{Al,Si})_2 -$ $\text{Si}_6\text{O}_{22}(\text{O,OH,F})_2$	Verona, Addington County, Ontario	2.9-3.4
Polysilicate	Albite	$\text{NaAlSi}_3\text{O}_8$	Bancroft, Ont.	2.60-2.61
	Labradorite	$\text{NaAlSi}_3\text{O}_8$ (30-50%) $\text{CaAl}_2\text{Si}_2\text{O}_8$ (70-50%)	Essex County New York	2.68-2.72
	Microcline	$\text{K AlSi}_3\text{O}_8$	Bathurst, Ontario	2.54-2.57
	Anorthoclase	$(\text{Na,K})\text{AlSi}_3\text{O}_8$	Larvik, Norway	2.57-2.60
Mica	Muscovite	$\text{K Al}(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$	Upton County Georgia	2.76-3
	Phlogopite	$\text{K Mg}_3(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$	Godfrey, Ontario	2.78-2.85
	Biotite	$\text{K}(\text{MgFe})_3(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$	Quebec	2.7-3.1

* Except for the composition of hornblende, these compositions and specific gravity values were obtained from Dana(13). The composition of hornblende was reported by Bragg (7).

B. Fractionation of the Minerals

All of the minerals listed in table 4, except the micas, were crushed in a jaw-type crusher and further reduced in size in a disc pulverizer. The micas were split into sheets and cut into pieces about one square centimeter in area. All of the minerals were pulverized for four or five days in a porcelain ball mill with quartzite balls.

The ground minerals were separated successively at the following approximate diameters in water using Stokes' Law for the calculation of settling time and the average specific gravity reported in table 4, 20.0, 15.5, 11.0, 6.5, 2.0 and 0.2 microns. The separations above 2 microns were accomplished by shaking the ground mineral in water and syphoning off the finer particles at the proper time. Fractionation at the 0.2 micron level was effected in a Sharples' supercentrifuge running at a speed of 36000 revolutions per minute and delivering 850 milliliters of suspension per minute at about 26 degrees C. As every mineral appeared to undergo some mechanical breakdown due to shaking, decantation was continued until the rate of breakdown was relatively constant. Even after 30 decantations at the 2 micron level the breakdown of biotite persisted. The fraction of each mineral less than 2 microns in diameter was passed through the supercentrifuge nine to

eleven times.

No dispersing agent was used in the fractionation. Only labradorite and hornblende would not remain dispersed on shaking. Labradorite flocculated when first placed in water but after syphoning off the supernatant liquid a few times good dispersion was obtained. In the case of hornblende separations at 20 and 15.5 microns were the only ones made, and it was noted that the pH of the solution was still above 8.5 - 9.0 after 16 decantations.

Microscopic examination of the 20 to 15.5 micron fraction of all minerals except the micas and hornblende, showed that some particles between 20 and 30 microns in diameter still remained. These larger particles were for the most part long and slender. The size range for the three mica samples appeared to be about 50 to 30 microns and for hornblende, 25 to 2 microns. The 11 to 6.5 micron fraction checked very well except the upper limit for the micas appeared to be about 25 microns and the lower limit about 12 microns. An appreciable quantity of this fraction of muscovite was as small as 1 micron. Only the upper size limit of the 2 to 0.2 micron fractions was checked. In all cases except for biotite the fractionation appeared to be effected at 2 microns. Biotite contained some flakes as large as 5 microns, but as this sample was shaken and syphoned

30 times, it is unlikely that this could be attributed to inadequate fractionation. It appears that numerous very thin plates were split off in the shaking treatment of the biotite.

C. Experimental Methods

1. Effect of Particle Size on Base Release

The method used in the study of the relationship of particle size and base release from minerals was a modification of a method used by Graham (19). He used an acid clay suspension as a weathering agent for primary minerals. In this study it was thought that a method could be devised to more nearly approximate soil conditions and also eliminate any release of bases that might be caused by shaking the mineral-colloid mixture. Accordingly, duplicate samples of the fractionated minerals were treated as follows: (1) mixed with hydrogen saturated bentonite; (2) leached with neutral, molar ammonium acetate; (3) resaturated with hydrogen using .05 M. acetic acid, and (4) allowed to stand in a humid incubation chamber. The leaching and resaturation with hydrogen were repeated at intervals.

Porcelain filtering crucibles with medium porous bottoms and a capacity of 40 cubic centimeters were used to contain the sample mixtures. It was necessary to add some filtering aid to the bentonite-mineral mixtures. Acid washed quartz,

11 to 50 microns in diameter, proved to be satisfactory. A mixture of 4 grams of mineral, 4 grams bentonite and 6 grams quartz was found to have reasonable filtering qualities. About 1 gram of 11 to 50 micron quartz was first placed in the bottom of the crucibles succeeded by the mineral-bentonite-quartz mixture. Approximately 4 grams of the acid washed quartz which was retained between 10 and 60 mesh screens, was placed on top. A small filter paper was wedged in over the contents to prevent the sample being disturbed during leaching operations. The blanks were treated similarly except the mineral was replaced by an additional 4 grams of quartz.

Each incubation chamber consisted of a well insulated outer wooden box which contained a second copper box. The samples were placed on open shelves in the copper box and a large pan of distilled water was placed on the bottom to decrease evaporation from the samples. Two identical incubation chambers were used and these were stored in a constant temperature room with an average temperature of 26 degrees C.

A supply of "Volclay" bentonite was obtained from the American Colloid Company. It was dispersed in water and allowed to settle for several days to allow the impurities to settle. The supernatant suspension was then saturated

with hydrogen by slowly passing it through a column containing the exchange resin "Amberlite", a method recommended by Stout (53). The hydrogen saturated bentonite suspension had most of the water removed by suction through a porous container and finally was dried on a hot plate. The dried bentonite was then ball milled for short periods and the material less than 100 mesh was removed by dry sieving. The exchange capacity of the bentonite was determined by titrating the hydrogen replaced from the hydrogen saturated colloid by neutral, normal barium acetate. It was found to be 72 milliequivalents per 100 grams.

It would have been desirable to leach the samples with a dilute acid and thus avoid the introduction of the ammonium ion. In a series of experiments with acetic acid it was found that 1500 milliliters of normal acetic acid were required to displace as much calcium from a bentonite-quartz mixture contained in a filtering crucible as was removed by 500 milliliters of normal ammonium acetate. The solvent action of this concentration of acetic acid precluded its use.

Two silt fractions from each of the minerals except hornblende, and the coarse clay fraction of all minerals were investigated in this experiment. The fractions selected were those portions of the minerals between the

approximate diameters listed in table 5. Each of the ammonium acetate leachates were analyzed for the principal bases likely to be present. The acetic acid leachates were discarded except after the third leaching at 70 days.

Table 5

Size Fractions of Minerals Investigated

	Coarse Silt (Microns)	Fine Silt (Microns)	Coarse Clay (Microns)
Feldspars, augite and olivine	20-15.5	11-6.5	2-0.2
Hornblende	25-2	-	Less than 2
Muscovite and phlogopite	50-30	25-6.5	2-0.2
Biotite	50-30	25-6.5	5-0.2

2. Effect of Ca:H Ratio on Base Release

This experiment was designed to study the relationship between the rate of base release from minerals and different degrees of calcium saturation of the exchange complex. The method employed was the same as that of the preceding experiment except for the substitution of the following leaching solutions for the .05 M. acetic acid: (1) .05 M. acetic acid and .05 M. calcium acetate solution, (2) .05 M. acetic acid and 0.1 M. calcium acetate solution, (3) .05 M. calcium acetate solution. These treatments will be referred to

hereafter as the 1:1 Ca:H, 2:1 Ca:H and Ca saturated treatments, respectively.

The coarse clay fractions of all of the minerals were used in this experiment for the 1:1 Ca:H treatment. For the 2:1 Ca:H and the calcium saturated treatments the experiment was restricted to microcline, muscovite, biotite, albite and augite. The preceding experiment on particle size included hydrogen saturated bentonite and as all of the samples were leached at the same time intervals in both experiments these samples were not repeated in this experiment. For purposes of evaluating bentonite as a weathering agent, 4 gram samples of the clay size fraction of each of the minerals were mixed with 10 grams of the 11 to 50 micron quartz and received the same treatment as was used in the experiment on particle size.

3. Effect of Temperature on Base Release

The effect of temperature was observed on the coarse clay fractions of microcline and muscovite. The samples were treated the same as in the particle size experiment except for the temperature of incubation. Duplicate samples of each mineral were incubated at 7, 16 and 41 degrees C. in desiccators partially filled with distilled water. In this experiment the samples appeared to have a higher moisture content than the samples contained in the larger incubators.

4. Effect of Electrodialysis on Base Release

The effect of electrodialysis was observed on the coarse clay fractions of microcline, muscovite, biotite and olivine. In this experiment 8 grams of each mineral fraction was wrapped in a filter paper and placed in a filtering crucible. They were leached with 1 liter of molar ammonium acetate previous to dialysis in order to displace the exchangeable ions which might be present.

The dialysis apparatus consisted of four similar units. The anode and cathodes consisted of circular platinum and copper wires respectively, one end of each being sealed into a glass tube. In each case they were connected to the electrical circuit by a mercury junction. The cathode chamber consisted of a 250 ml. beaker with an opening in the side about 2 inches from the bottom. The anode chamber was a 40 ml. filtering crucible with a porous bottom. It was lengthened to about 6 inches by joining a glass tube of the same diameter to it by means of a wide rubber band. The anode chamber was closed with a 3 hole stopper which contained the anode and two glass tubes. The apparatus was suspended by clamps from four ring stands. The cathode chamber was suspended over a 1 litre beaker. The cathode was placed in the bottom of the chamber and encircled the bottom of the anode chamber. The distance between the anode

and cathode in each case was very nearly the same - about 2 inches. Distilled water was slowly admitted to the anode chamber containing the sample, through a glass tube inserted in the stopper of the anode chamber and excess water was removed by an outlet tube. It was not necessary to add water to the cathode chamber as diffusion and/or electrophoresis provided ample overflow. A potential of approximately 100 volts was maintained and the cathode chamber was cleaned out at intervals of 7 days. The experiment was carried on for 5 weeks.

D. Analytical Procedures

1. Total Bases

To determine total bases the 2 to .2 micron fractions of each of the minerals and an unfractionated portion were treated with hydrofluoric acid using a method described by Willard and Diehl (59, p. 276). Iron, aluminum and manganese were removed according to Willard and Furman (60, p. 394) and the filtrate concentrated to a known volume. Calcium was precipitated in an aliquot by the standard oxalate procedure (60) and titrated with standard potassium permanganate. Magnesium was precipitated as the dibasic phosphate and completed volumetrically (44). Potassium was determined

colorimetrically on a fresh aliquot by the dipicrylamine method (38) after the ammonium salts were destroyed. Sodium was precipitated as sodium magnesium uranyl acetate and weighed according to the procedure outlined by Peech and associates (44). A separate sample was used for sodium without having the sesqui-oxides removed.

2. Exchangeable Bases

The ammonium acetate and other extracts were analyzed as outlined by Peech and associates (44, p. 8). They were taken to dryness, treated with a mixture of hydrochloric and nitric acids, transferred to 50 ml. beakers, evaporated to dryness, ignited in a furnace controlled at 400 degrees C. and taken up in 25 ml. of 0.1 N. nitric acid.

The major bases contained in each solution were determined on aliquot solutions by the following methods: Potassium by the dipicrylamine method outlined by Lawton (38); sodium by the micromethod outlined by Peech and associates (44) except the precipitated sodium magnesium uranyl acetate was weighed; calcium by the oxalate method (44); magnesium by the thiazole yellow method of Drosdoff and Nearpass (16) using twenty minutes to develop the color and a 515 filter. Satisfactory agreement was obtained between this method and the thiazole yellow method of Mikkelsen, Toth and Prince (42) and the standard dibasic phosphate method (44).

IV. EXPERIMENTAL RESULTS

A. Total Bases in Minerals

The analyses of total bases in the minerals studied are included in table 6. Ca, Mg, Na and K are reported both on a percentage basis and as millimoles per 100 grams for the 2 to .2 micron fraction of all of the minerals. The major bases for the ground but untreated minerals are also included in table 6. The analyses indicate that the minerals conform reasonably well to the theoretical compositions indicated in table 4.

Table 6

Total Bases in Minerals

Mineral	Frac- tion	Percent composition				Millimoles /100 g.			
		Ca	Mg	Na	K	Ca	Mg	Na	K
Olivine	C*	.15	24.46	.07	.76	4	1006	3	19
	U**		28.71				1180		
Augite	C*	14.07	3.74	.26	.54	351	154	11	14
	U**	15.51	3.83			387	157		
Horn- blende	C*	14.59	4.59	.72	.49	364	189	31	13
	U**	15.36	4.85			383	199		
Albite	C*	2.70	.39	5.36	1.38	67	16	233	35
	U**			6.02	1.02			262	26
Labra- dorite	C*	8.05	1.34	3.27	1.05	201	55	142	27
	U**	8.02		3.47		200		151	
Micro- cline	C*	.12	1.20	1.66	10.38	3	49	72	266
	U**				11.22				287
Anortho- clase	C*	2.50	.86	4.80	3.04	62	35	209	78
	U**			4.82	3.13			210	80
Musco- vite	C*	0.0	.70	.44	8.10	0	29	19	207
	U**				8.77				224
Phlogo- pite	C*	0.0	16.52	.02	8.27	0	679	1	212
	U**		16.56		8.96		681		229
Biotite	C*	0.0	10.00	.28	7.55	0	411	12	193
	U**		10.15		8.23		417		211

* Coarse Clay

** Unfractionated

The composition of several minerals changed appreciably by hydrolysis during fractionation. Olivine lost about 15 percent of its total Mg. Augite lost almost 10 percent of the original Ca content whereas Mg was relatively unchanged. Possibly the amount of Ca in solution was sufficient to raise the pH enough to prevent appreciable loss of Mg from augite during fractionation. Hornblende lost about 5 percent of its Ca and Mg by hydrolysis of the ground mineral. Albite lost about 11 percent of its Na content and gained considerably in K. This is difficult to explain unless that portion of the mineral containing more K accumulated in the finer fractions. Labradorite and anorthoclase showed little change in composition. Microcline lost $7\frac{1}{2}$ percent of its total K content.

The micas behaved similarly, all of them lost approximately 8 percent of their original K content. As they were ground to about the same fineness, this could be expected. The Mg in both biotite and phlogopite was not affected by the water treatment, probably because of the increase in pH resulting from the hydrolyzed K.

B. Effect of Particle Size on Base Release

The data obtained from the particle size experiment are presented in table 7. Much of this data is shown graphically in figure 1. The initial release of bases prior to incubation

is not included in the graphs. For convenience the minerals will be discussed in the divisions shown in table 1.

1. Orthosilicate Division

Olivine was the only member of this division that was studied. The rate of release of its Mg was found to be much higher than the release of bases from any other mineral. The two silt sizes of olivine did not show much difference in the quantity of Mg released but for the clay fraction the rate was nearly doubled. A second ammonium acetate leaching immediately following the first leaching of the olivine clay fraction incubated for 70 days, caused a further release of 3 millimoles of Mg. This would indicate some solution effect by the ammonium acetate leachate. The .05 M. acetic acid had a much greater effect causing the release of between 14 and 27 millimoles of Mg, the amount released apparently being a function of the time of contact.

2. Metasilicate Division

Augite and hornblende were the two minerals of this division that were included in the investigation. For both of these minerals decreasing particle size caused a marked increase in the release of bases. After 70 days the release of Mg in both cases decreased to a very small value but continued to be released at an appreciable rate. For the coarse

Table 7

Millimoles of Bases Released at Successive Intervals from
Fractionated Minerals Mixed with H-Bentonite
(Millimoles per 100 g.)*

Mineral	Base	Coarse Silt					Fine Silt					Coarse Clay				
		(Interval in days)					(Interval in days)					(Interval in days)				
		0	35	35	134	35	0	35	35	134	35	0	35	35	134	35
Olivine	Mg	8.2	23.7	19.2	15.0	3.5	12.8	27.1	16.3	10.1	2.4	40.6	51.9	27.2	10.9	12.4
Augite	Ca	3.0	.9	.5	.4	.5	3.2	1.6	.6	1.2	.2	39.6	8.4	2.9	4.7	1.1
	Mg	3.5	.1	.0	.1	.1	4.0	2.0	.3	.3	.0	6.1	10.9	3.2	2.2	.3
Horn- blende	Ca	44.7	1.9	.6	.9	.3						76.7	4.5	1.0	1.6	.5
	Mg	3.5	6.9	.8	.3	.1						5.3	11.8	2.3	1.3	.3
Albite*	Na	4.0	.8	.4	1.3	.2	3.4	3.4	1.4	5.9	.0	33.2	10.3	3.6	4.8	.8
	K	5.2	.4	.4	.4	.2	5.4	.6	.4	.8	.2	13.3	4.2	1.2	1.2	.0
Labra- dorite	Na	.7	.3	.2	.7	.1	.6	.4	.6	1.0	.0	2.8	1.3	.9	1.7	.9
	Ca	3.2	1.0	1.9	1.0	.2	4.0	1.8	1.7	1.9	.4	15.5	4.5	2.4	3.4	1.9
Micro- cline	K	.6	.2	.1	.1	.1	.7	.3	.1	.2	.1	6.8	2.8	.8	.6	.4
Anortho- clase	K	1.0	1.2	.2	.1	.1	1.3	1.4	.2	.2	.1	3.8	1.3	.7	.6	.2
	Na	2.4	5.4	.7	.7	.0	3.3	3.9	.7	1.1	.0	8.4	1.5	1.0	1.0	.5
Musco- vite	K	9.4	4.3	.6	.4	.3	15.2	5.3	.9	.6	.2	37.6	18.8	8.8	1.1	1.8
Phlogo- pite	K	1.3	.8	.7	.7	.3	1.6	.9	.5	.5	.3	2.6	1.4	.5	.2	.1
	Mg	13.3	12.8	3.5	2.3	.6	16.4	16.0	4.4	2.4	.5	24.5	25.9	3.9	1.0	.4
Biotite	K	.8	.6	.3	.1	.1	.8	.8	.3	.3	.1	2.3	1.6	.8	.4	.1
	Mg	3.0	.8	.1	.1	.0	3.4	1.1	.3	.2	.0	7.4	6.6	1.8	.5	.0

*Release data for albite are reported as millimoles /1000 g.

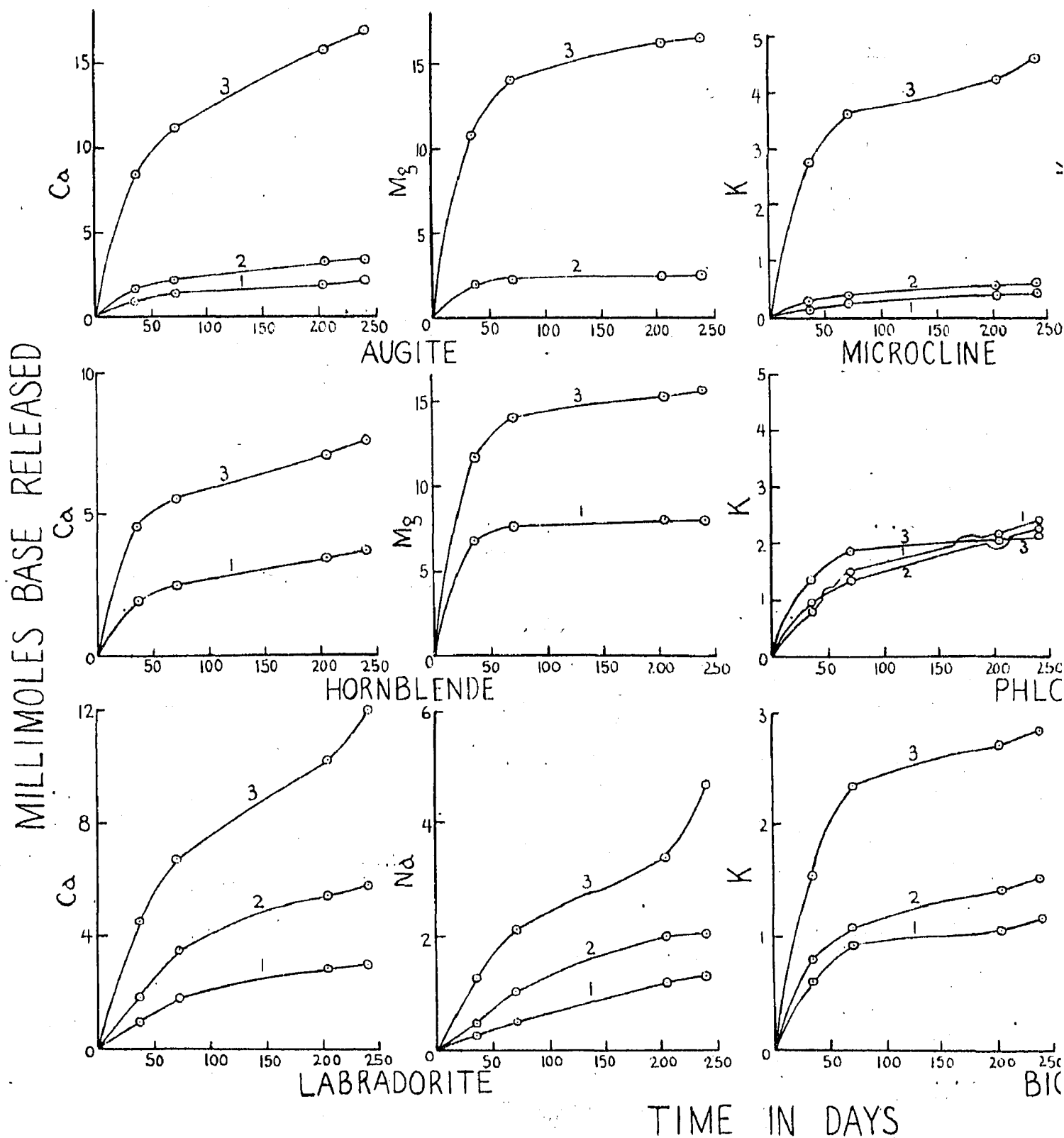
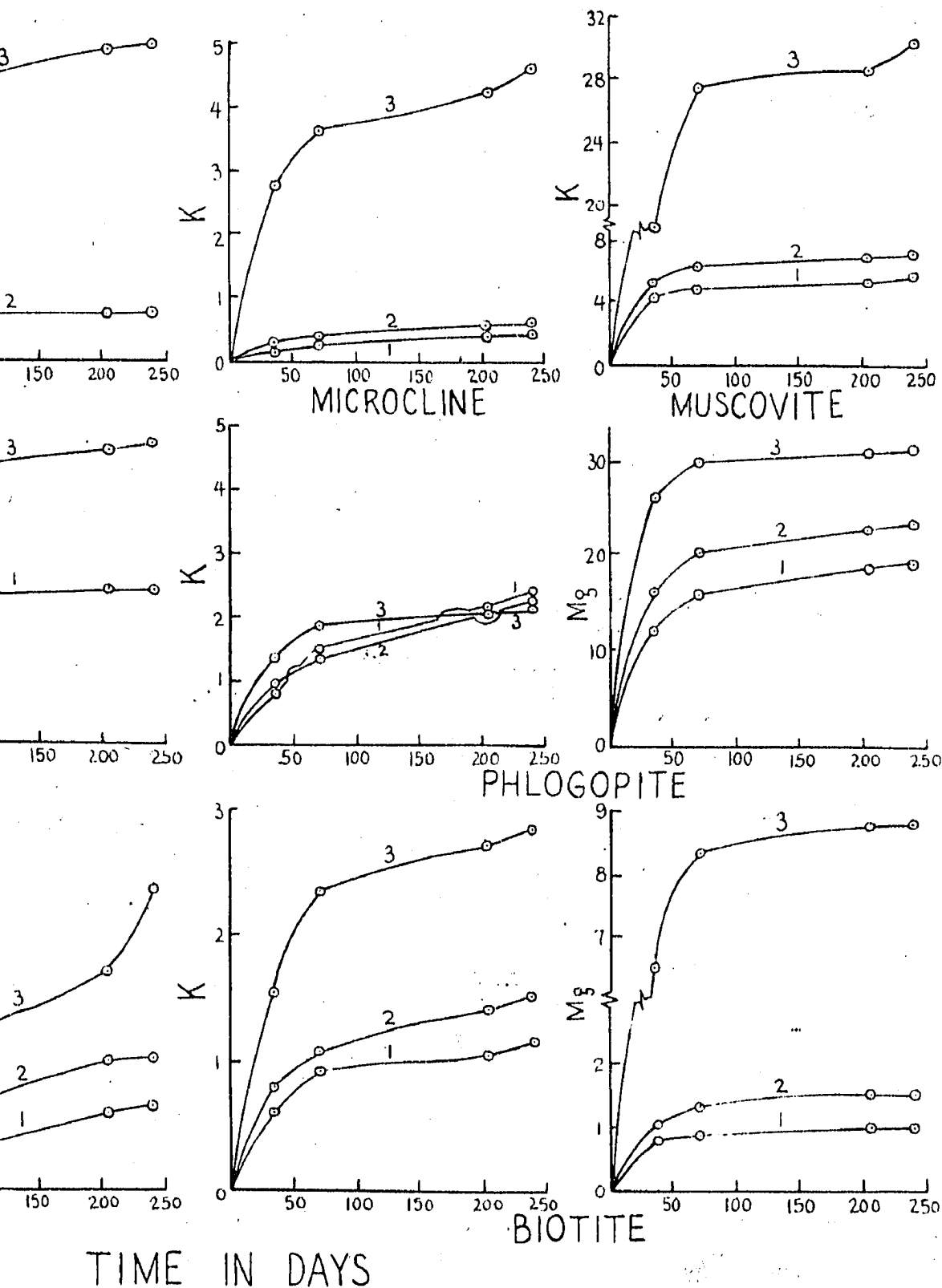


Figure 1. Effect of Particle Size on the Rate of Release of Bases f



KEY
 1. COARSE SILT
 2. FINE SILT
 3. COARSE CLAY

on the Rate of Release of Bases from Minerals Incubated with H-Bentonite.

clay fraction the ratio of Ca to Mg at the end of the third and fourth leaching intervals tended to approach the molecular ratio of these two elements in the original mineral.

3. Disilicate Division

Microcline, anorthoclase, albite and labradorite belong to this division of minerals. The release of bases from these minerals increased with decreasing particle size except for Na release from anorthoclase. For no apparent reason the release of Na from the two silt sizes of anorthoclase during the first 35 day interval was abnormally high. Subsequent release of Na decreased with increased particle size.

The graphs for albite and anorthoclase are not shown in figure 1. Except for Na in anorthoclase they closely approximate the graphs of microcline shown in figure 1 in form and relative differences in base release due to particle size. From figure 1 it can be seen that labradorite is weathering at a much faster rate than microcline. The relative effect of particle size is more pronounced in the case of microcline than for labradorite. Ca is released from labradorite faster than the molecular ratio of Na to Ca in the original mineral would indicate.

4. Mica Division

The effect of particle size on the micas was somewhat variable. The release of K from muscovite and biotite was not greatly different for the coarse and fine silt fractions. A much greater release of K was obtained from the coarse clay fraction of muscovite than from the silt fractions. For biotite the difference between the release of K from the silt sizes and coarse clay fraction were not as marked. This is probably due to the larger size limit of the clay fraction of biotite as shown in table 5.

The release of Mg from phlogopite and biotite was proportionally greater than the ratio of total K:Mg in these minerals would indicate. After 70 days incubation the release of Mg rapidly declined. In the final leaching the ratio of K:Mg in phlogopite became about 1:3. Biotite almost ceased releasing Mg. During the last leaching interval there was no appreciable difference in the amount of K or Mg released from the three size fractions of biotite and muscovite.

C. Effect of Ca- and H-Saturation on Base Release

The data from this experiment are included in tables 8 and 9 and plotted in figure 2.

Table 8

Millimoles of Bases Released at Successive Intervals from Coarse
Clay Fractions of Minerals Mixed with H-Bentonite,
Ca-H-Bentonite and Quartz Alone
(Millimoles per 100 g)

Mineral Base		H-Bentonite (Interval in days)					1:1 Ca:H-Bentonite : (Interval in days) :					No Bentonite (Interval in days)				
		0	35	35	204	35	35	35	204	35	35	35	35	204	35	91
Olivine	Mg	40.6	51.9	27.2	10.9	12.4	12.1	5.8	10.4	4.5	8.2	8.9	3.9	2.9	2.6	
Augite	Ca	39.6	8.4	2.9	4.7	1.1					2.0	1.1	1.9	.6	.9	
	Mg	6.1	10.9	3.2	2.2	.3	3.8	.7	.8	.0	2.8	1.8	1.2	.8	.5	
Horn- blende	Ca	76.7	4.5	1.0	1.6	.5					.8	.9	.5	.2	.4	
	Mg	5.3	11.8	2.3	1.3	.3	4.0	.9	.9	.2	2.0	2.1	1.4	.7	.4	
Albite	Na	3.3	1.0	.4	.5	.1	.5	.0	.1	.1	.4	.4	.3	.2	.2	
	K	1.3	.4	.1	.1	.0	.1	.0	.0	.0	.2	.2	.2	.2	.1	
Labra- dorite	Na	2.8	1.3	.9	1.7	.9	.7	.4	.5	.3	.5	.5	.6	.3	.5	
	Ca	15.5	4.5	2.4	3.4	1.9					1.6	3.4	3.0	1.4	1.4	
Micro- cline	K	6.8	2.5	.7	.6	.3	1.6	.5	.2	.2	2.0	1.2	.9	.6	.5	
Anortho- clase	K	3.8	1.3	.7	.6	.2	1.4	.3	.2	.1	1.0	.7	.5	.3	.3	
	Na	8.4	1.5	1.0	1.0	.5	3.7	.5	.7	.4	1.1	.9	.7	.3	.5	
Musco- vite	K	37.6	18.8	8.8	1.1	1.8	12.1	5.5	6.5	.4	11.6	7.6	6.8	3.4	3.5	
Phlogo- pite	K	2.6	1.4	.5	.2	.1	.7	.3	.2	.2	1.2	1.1	.7	.5	.3	
	Mg	24.5	25.9	3.9	1.0	.4	7.7	2.0	2.2	1.7	10.2	8.8	6.0	2.8	.4	
Biotite	K	2.3	1.6	.8	.4	.1	.7	.3	.1	.1	.6	.6	.6	.5	.5	
	Mg	7.4	6.6	1.8	.5	.0	.8	.2	.2	.1	1.8	1.1	.8	.4	.0	

Table 9

Millimoles of Bases Released at Successive Intervals from Coarse
Clay Fractions of Minerals Mixed with Bentonite of
Different Degrees of Ca-and H-Saturation
(Millimoles per 100 g)

Mineral Base		H-Bentonite				:1:1 Ca:H-Bentonite				:2:1 Ca:H-Bentonite				Ca-Bentonite				:
		(Interval in				ite (Interval in				:(Interval in days):				:(Interval in days):				:
		days)				:days)				:				:				:
		35	35	134	35	35	35	134	35	35	35	134	35	35	35	134	35	:
Augite	Ca	8.4	2.9	4.7	1.1													
	Mg	10.9	3.2	2.2	.3	3.8	.7	.8	.0	3.2	.7	.4	.0	1.2	.4	.6	.0	
Albite	Na	1.0	.4	.5	.1	.5	.0	.1	.1	.6	.3	.3	.0	.3	.2	.4	.0	
	K	.4	.1	.1	.0	.1	.0	.0	.0	.2	.1	.1	.0	.1	.0	.1	.0	
Micro- cline	K	2.5	.7	.6	.3	1.6	.5	.2	.2	1.4	.6	.4	.2	1.1	.7	.4	.3	
Musco- vite	K	18.8	8.8	1.1	1.8	12.1	5.5	6.5	.4	10.9	5.7	4.5	2.0	8.3	4.4	3.9	1.8	
Biotite	K	1.6	.8	.4	.1	.7	.3	.1	.1	.7	.2	.1	.1	.5	.2	.1	.1	
	Mg	6.6	1.8	.5	.0	.8	.2	.2	.1	.7	.0	.1	.0	.3	.1	.0	.0	

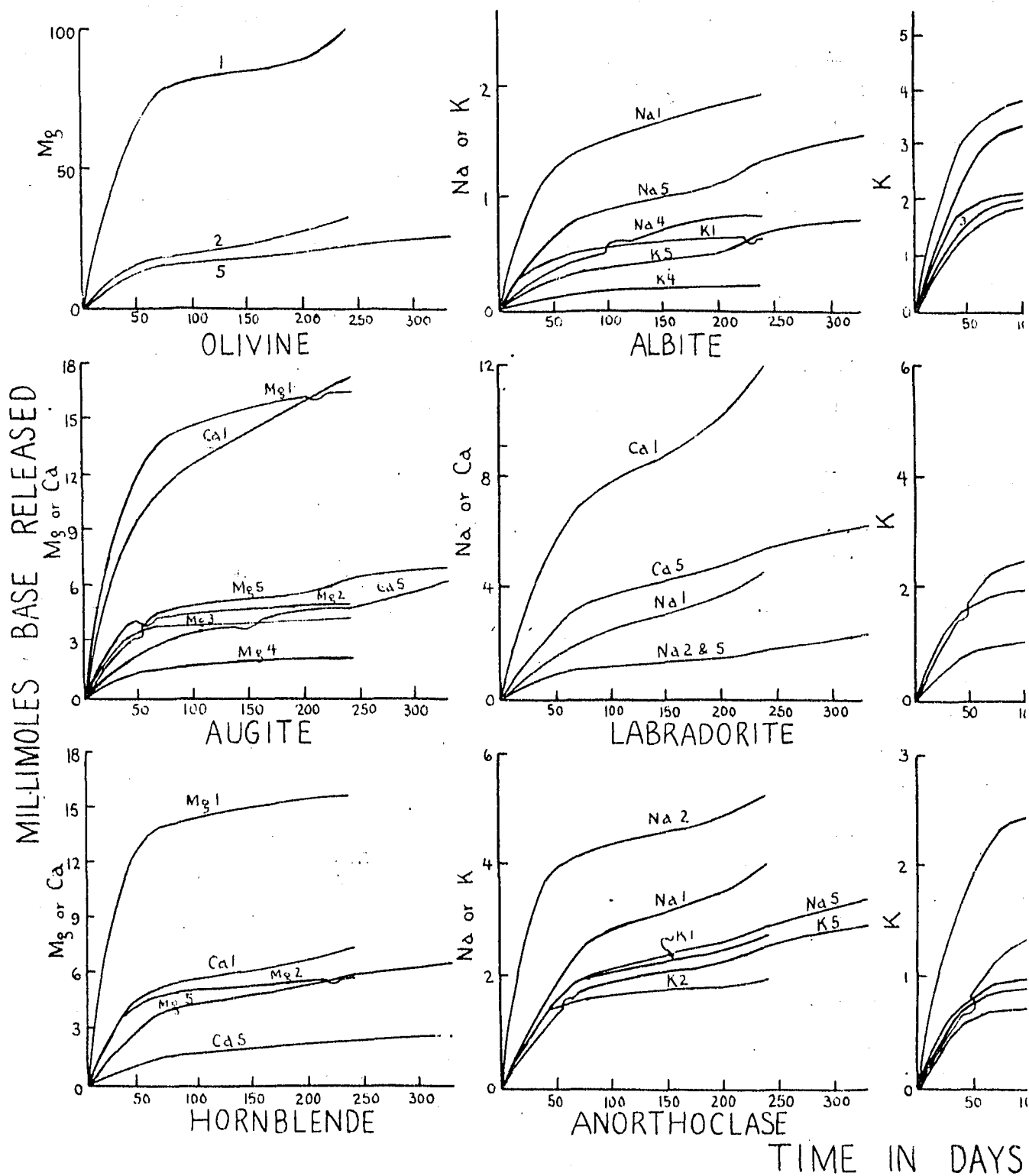
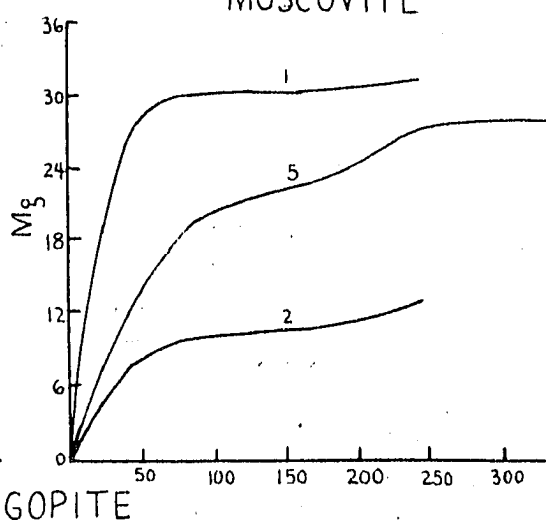
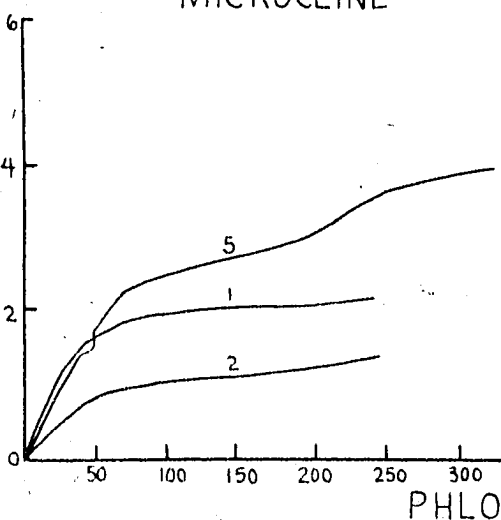
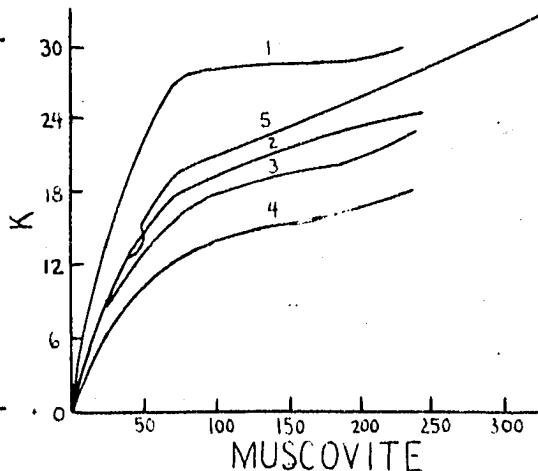
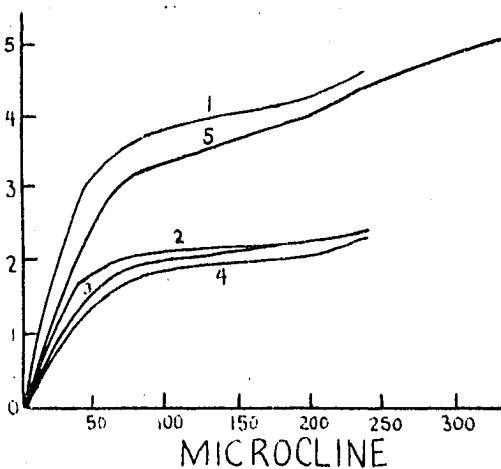
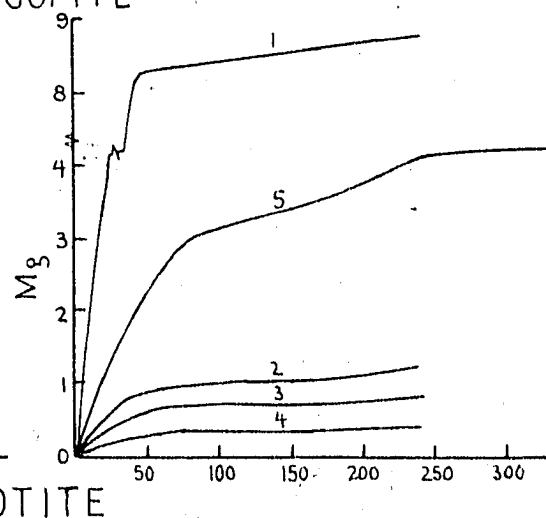
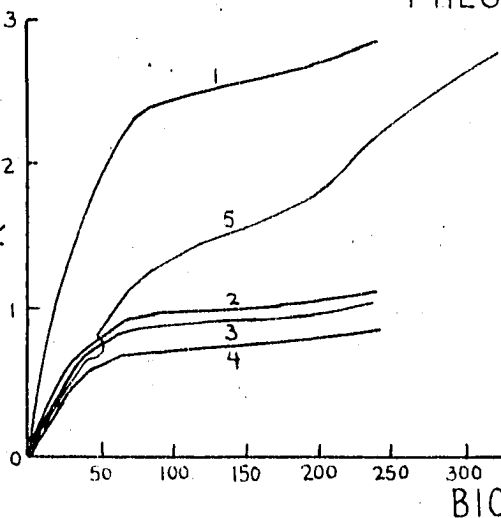


Figure 2. Release of Bases at Successive Intervals from Coarse Cls 2:1 Ca:H-Bentonite, Ca-Bentonite and Quartz Alone.



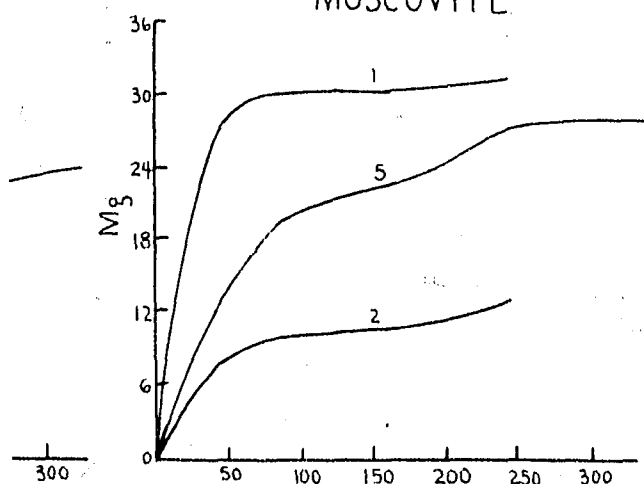
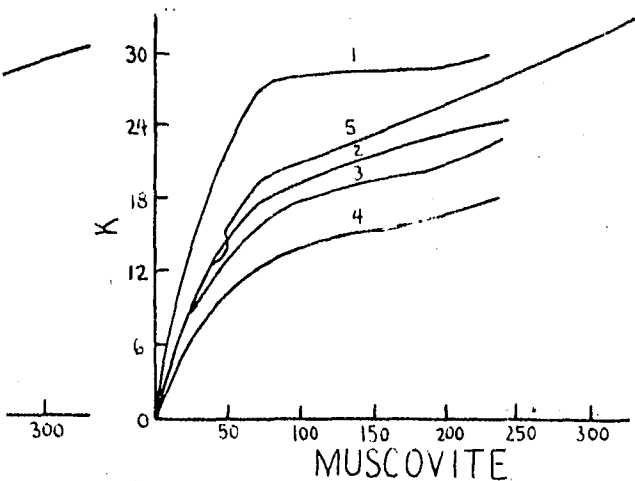
Key

1. H-Bentonite Treatment
2. 1:1 Ca:H-Bentonite
3. 2:1 Ca:H-Bentonite
4. Ca-Bentonite Treatment
5. Quartz Treatment



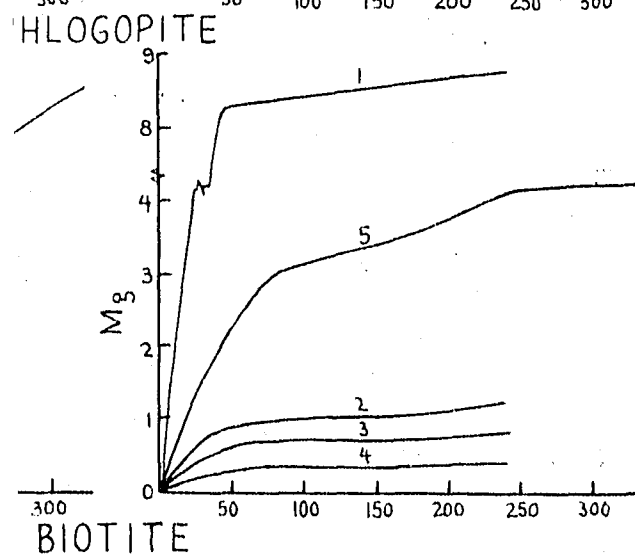
IN DAYS

Coarse Clay Fractions of Minerals Mixed with H-Bentonite, 1:1 Ca:H-Bentonite, one.



Key

1. H-Bentonite Treatment
2. 1:1 Ca:H-Bentonite Treatment
3. 2:1 Ca:H-Bentonite Treatment
4. Ca-Bentonite Treatment
5. Quartz Treatment (No Bentonite)



Minerals Mixed with H-Bentonite, 1:1 Ca:H-Bentonite,

From tables 8 and 9 and figure 2 it can be seen that in every instance except for the release of Na from anorthoclase the partial substitution for Ca for H on the bentonite caused a decrease in the quantity of base released. The Ca-saturated samples released fewer bases than the partially Ca-saturated samples. The decrease was less pronounced for the feldspars and muscovite.

Table 8 and figure 2 show that the presence of bentonite did not affect all of the minerals to the same extent. In general the potash feldspars and micas showed the smallest increases in bases released by the addition of H-bentonite.

D. Effect of Temperature on Base Release

The data showing the effect of temperature on base release are shown in table 10. The accumulative total K released with time is plotted against temperature in figure 3.

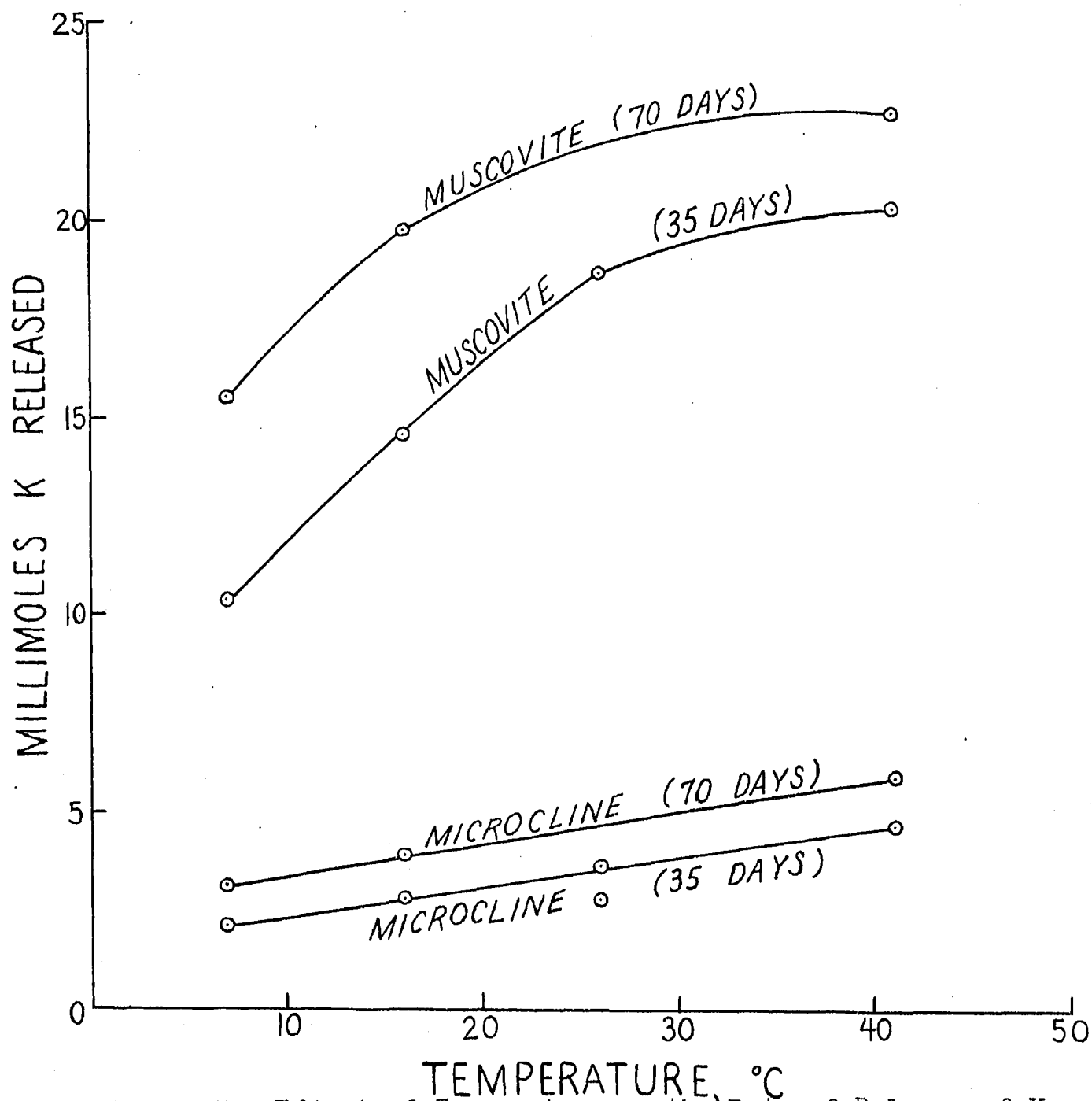


Figure 3 - Effect of Temperature on the Rate of Release of K from the Coarse Clay Fractions of Microcline and Muscovite by Incubation with H-Bentonite

Table 10

Effect of Temperature on Base Release from the Coarse
Clay Fractions of Microcline and Muscovite

(Millimoles per 100 grams)

Mineral	Incubation period (days)	Temperature (degrees C.)			
		7	16	26*	41
Microcline	0-35	2.1	2.8	2.8	4.7
	35-70	1.0	1.1	.8	1.3
Muscovite	0-35	10.4	14.6	18.8	20.4
	35-70	5.1	5.2	8.8	2.4

* Data from table 7. These samples were not incubated at the same relative humidity as was employed at the other temperatures.

The release of K from microcline with increase in temperature increases linearly if the data at 26 degrees C. are neglected. This may indicate that a solubility relationship is involved. For muscovite the K released with time tends to reach a maximum value which would indicate that some factor limits the release of K. Possibly, if the K moves out from the crystal lattice, the rate of diffusion is the limiting factor.

E. Effect of Electrodialysis on Base Release

The data from the electrodialysis experiment are included in table 11 and are shown graphically in figure 4.

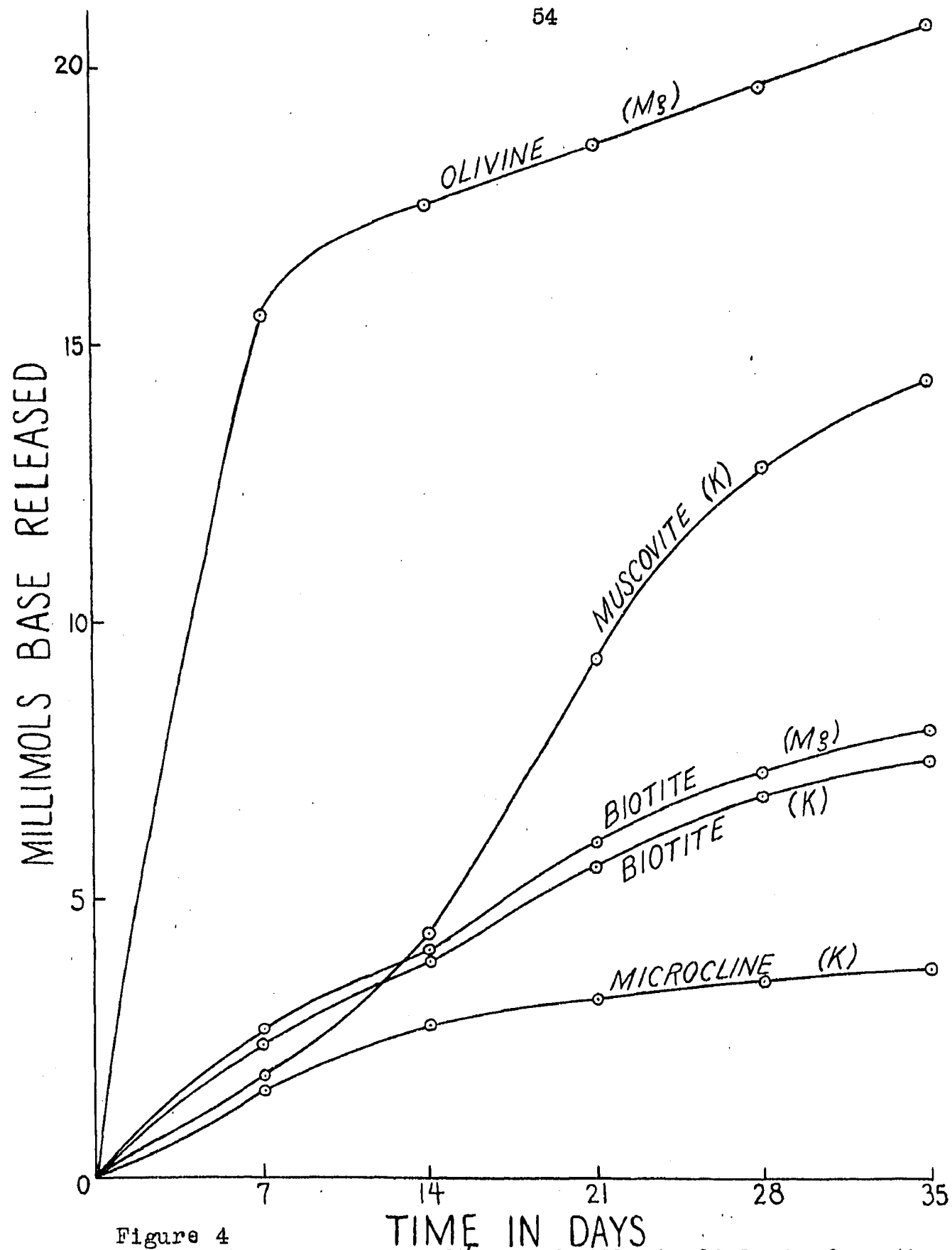


Figure 4
Rate of Release of K and/or Mg by Electro dialysis from the
Coarse Clay Fractions of Four Minerals

Table 11

Effect of Electrodialysis at 100 Volts
on Base Release

(Millimoles per 100 grams)

Mineral	Base	Interval in days					
		0*	0-7	7-14	14-21	21-28	28-35
Microcline	K	4.58	2.04	.68	.45	.33	.23
Muscovite	K	43.51	1.81	2.56	5.01	3.47	1.55
Biotite	K	1.12	2.36	1.54	1.70	1.28	.63
	Mg	2.30	2.62	1.40	2.00	1.28	.78
Olivine	Mg	12.19	15.52	2.00	1.10	1.01	1.17

These bases were removed by ammonium acetate solution prior to electrodialysis.

Of all the minerals electrodialyzed the greatest release of bases was obtained from olivine. After 14 days the rate of release of Mg was constant. For muscovite a constant rate of release of K may not have been attained in 35 days. At the completion of the experiment it was still releasing quite large quantities of K. From figure 3 it would appear that the release of K from muscovite was somewhat inhibited during the first 14 days. This may have been caused by the fixation of ammonia in the crystal lattice of muscovite during the ammonium acetate extraction. If this is the case both ammonia and K would be removed in the early stages of electrodialysis. The ammonia was not determined.

The rate of release of Mg and K from biotite diminished slightly during the second week. This may have been caused by an accumulation of iron on the anode side of the filtering

crucible, thus decreasing the diffusion rate of the bases. The accumulated iron was removed periodically. As Mg and K were removed in almost the same molar quantities from biotite and the ratio of Mg:K in the original mineral was 2:1, more K was removed than could be accounted for by solution of the mineral. Apparently K can be replaced from biotite independently of Mg.

Microcline tended to release K at a progressively decreasing rate. This may have been caused by the formation of a residual layer about the microcline particles as has been suggested by several workers (12) (2). It is also possible that K was replaced by H in the crystal lattice, and as more K was removed it became increasingly difficult for the H to replace it.

F. Solution Effect of Normal Ammonium Acetate and Twentieth Molar Acetic Acid

The solution effect of ammonium acetate was studied by releaching the coarse clay fraction of each mineral with 400 milliliters of N. ammonium acetate. This releaching was effected after the second incubation period. It was carried out immediately after the usual ammonium acetate leaching. The second ammonium acetate leachate from olivine contained about 3 millimoles of Mg. Muscovite and phlogopite released .2 millimole of K and Mg respectively and microcline over .1 millimole of K. These were the only measurable

quantities of bases released by any of the minerals during this second leaching.

The .05 M. acetic acid leachate following the ammonium acetate leaching referred to in the preceding paragraph, was analyzed for the principal bases present. The duplicate olivine leachates contained 14 and 27 millimoles of Mg. As the time of contact with acetic acid varied between samples, it is probable that this difference was due to the rate of leaching. The phlogopite leachate contained 2 millimoles of Mg and less than .2 millimole of K. Biotite and muscovite released about .4 and .2 millimole of K. The release of bases from the remaining minerals varied from about 0 to .2 millimole except for labradorite. The labradorite leachate contained about 1 and .2 millimole of Ca and Na, respectively.

V. DISCUSSION

The experimental results indicate that minerals decompose at appreciable and widely divergent rates. All minerals containing more than one principal base did not release these bases in the same relative proportion as might have been expected from their total analyses. Table 12 shows the loss of the principal bases of the coarse clay fraction of the minerals during the fractionation and leaching processes. The release data from the mixtures of minerals with H-bentonite are presented in the table.

Table 12

Release of Bases during Fractionation and Treatment
of the H-Saturated Coarse Clay Fraction of the
Mineral-Bentonite Mixtures
(Millimoles per 100 grams)

Mineral	Base	Original Base Content	Release by frac- tionation	Release at 0 days	Release in 240 days	Total Release
Olivine	Mg	1180	174	41	102	317
Augite	Ca	387	36	40	17	93
	Mg	157	3	6	17	26
Horn-	Ca	383	19	77	8	104
blende	Mg	199	10	5	16	31
Albite	Na	262	29	3	2	34
	K	26	9*	1	1	-
Labra-	Ca	200	0	16	12	28
dorite	Na	151	9	3	5	17
Micro-	K	287	21	7	5	33
cline						
Anortho-	Na	210	2	8	4	14
clase	K	80	2	4	3	9
Musco-	K	224	17	38	31	86
vite						
Phlogo-	Mg	681	2	24	31	57
pite	K	229	17	3	2	22
Biotite	Mg	417	6	7	9	22
	K	211	18	2	3	23

* Gain

From the data in table 12 it can be seen that olivine released about 27 percent of its original total Mg during fractionation and incubation with H-bentonite for 240 days. The same treatment caused the release of approximately 22 percent of the original bases in augite and hornblende. Of the feldspars labradorite released about 14 and 11 percent of its total Ca and Na, respectively; microcline released 11.5 percent of its K. Muscovite, phlogopite and biotite released about 38.5, 9.5 and 11 percent of their K, respectively. The total Mg content in phlogopite and biotite decreased nearly 8.5 and 5.5 percent, respectively.

Data for the release of bases from albite and anorthoclase during fractionation as shown in table 12 may not be comparable with the data for the other minerals. As suggested previously albite may have gained in potash feldspar during fractionation and this might explain the increase of 9 millimoles in K content of the coarse clay fraction. If this is so the content of sodium feldspar would be decreased by an amount corresponding to the increase in potassium feldspar.

The anorthoclase sample contained a dark mineral as an impurity. The sample came from Norway where it is commonly associated with augite (13). In the fractionation process this dark mineral may have hydrolyzed at a faster rate than

anorthoclase. The fractionated samples of anorthoclase became increasingly lighter colored with decrease in particle size except for the portion less than .2 microns in diameter. This fine clay fraction was quite dark in color. If the dark mineral had a less rigid structure than anorthoclase it is probable that grinding would result in fracture along the planes in which the dark mineral was situated. This would result in many of the particles having the dark mineral on the outer surface. The dark mineral may have contained appreciable quantities of Na and in the fractionation process the finer particles were in contact with water for progressively increased periods of time. Thus more Na could have been hydrolyzed from the finer particles of anorthoclase during fractionation. This might explain the high rate of release of Na from the silt fractions. Furthermore, the coarse clay fraction of anorthoclase did not appear to contain much, if any, dark mineral. The loss of but 2 millimoles of Na from the coarse clay fraction of anorthoclase as reported in table 12 could then be attributed to differences in content of the dark mineral.

Several minerals contained more than one base. The rates at which these bases were released were not identical as can be seen from table 13.

Table 13

Relative Rates of Release of Bases from the Minerals
Containing Two Principal Bases by Incubation
with H-Bentonite
(Molecular ratios)

Mineral	Ratio	Orig- inal Min.	Total* Release	Incubation Period (days)				
				0- 0	35- 35	35- 70	70- 204	204- 239
Augite	Ca:Mg	2.5	3.6	6.4	.8	.9	2.2	3.9
Hornblende	Ca:Mg	1.9	3.4	14.4	.4	.5	1.2	1.6
Albite	Na:K	10.1	- -	2.5	2.5	3.0	4.0	- -**
Labra- dorite	Ca:Na	1.3	1.6	5.6	3.4	2.8	2.0	2.2
Phlogo- pite	Mg:K	3.0	2.6	9.4	18.5	7.8	5.5	2.9
Anortho- clase	Na:K	2.6	1.6	2.2	1.2	1.5	1.8	2.0
Biotite	Mg:K	2.0	1.0	3.2	4.2	2.2	1.2	- -**

*These figures were obtained from table 12.

**The ratio is omitted in those instances where the release of either base was negligible.

The computations in table 13 indicate that as the length of the total incubation period was increased the ratio of the two bases released tended to approach the ratio of these two bases in the original mineral. Biotite and augite may be exceptions. Similar calculations for the mineral samples incubated with quartz showed the same trend but the ratios were more variable.

The rate of release of K from the principal K-bearing minerals investigated, is represented graphically in figure 5. The data for the coarse clay fraction incubated with H-bentonite were used. The accumulated release of K from

muscovite was more than 6 times as great as that of microcline. While anorthoclase contained about one third as much K as biotite and phlogopite, the K released was about the same. The increased rate of release of K for muscovite and microcline during the last 35 day interval may have been due to the acetic acid treatment removing accumulated sesquioxides.

The general form of the release curves in figures 1, 2 and 4 is the same for all of the minerals. A rapid initial period of base release tends to level off to a constant rate. Several workers (2)(12) have suggested that primary weathering products form a residual layer around the unweathered minerals. This may be the explanation for the decrease in the rate of base release with time from olivine, augite and hornblende, at least. These three minerals are similar in that divalent bases link the silica tetrahedra or chains together in the crystal lattice. It is not possible for monovalent H to replace the divalent bases without decomposing the minerals. If the residual iron, alumina, silica and bases were removed as weathering progressed, it is reasonable to expect that the minerals would continue to breakdown at a fairly constant rate. In the incubation experiments reported the bases were removed periodically but the removal of the other weathering products was not followed.

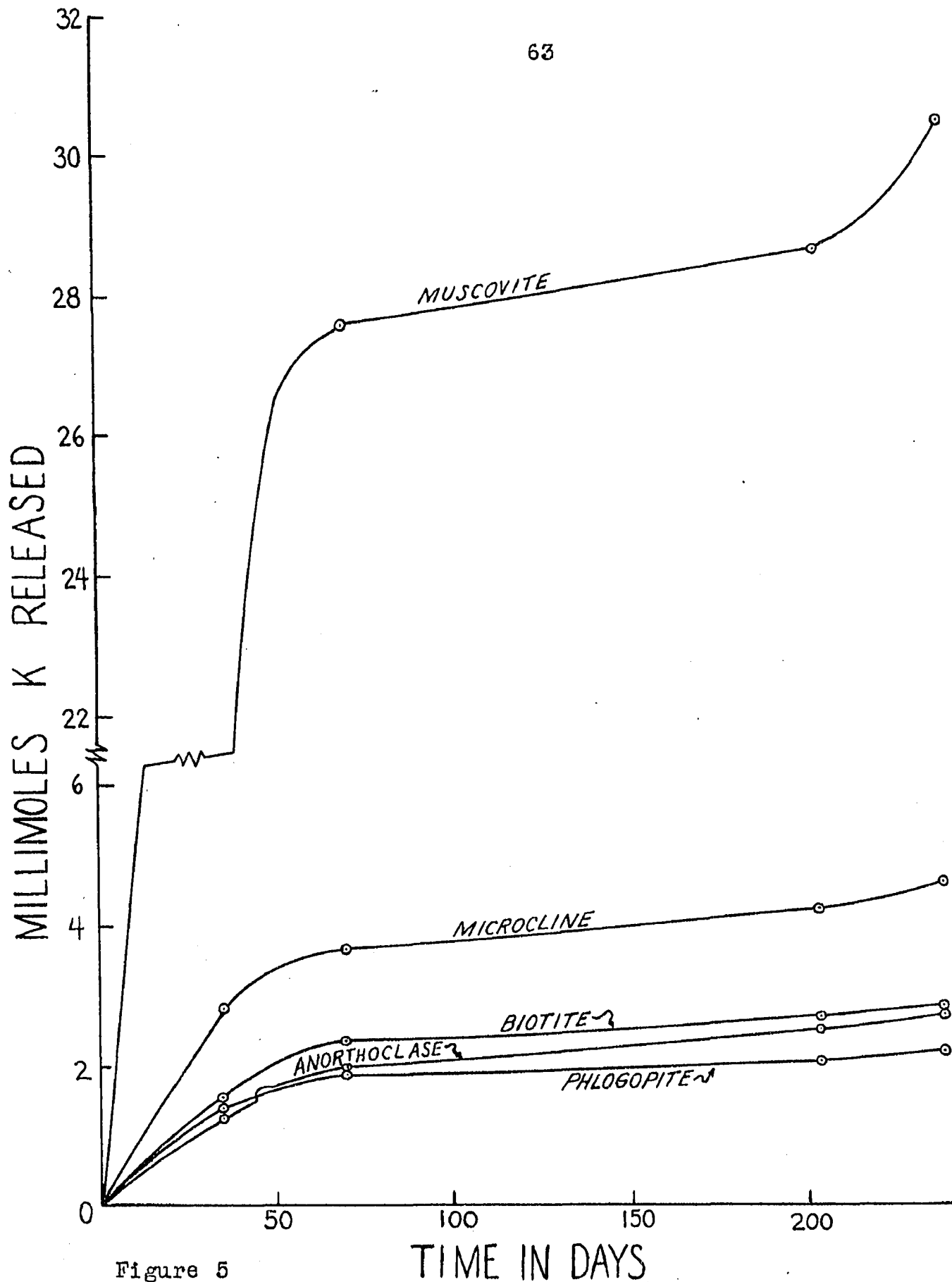


Figure 5
Rate of Release of K from the Coarse Clay Fraction of some
K-Bearing Minerals during Incubation with H-Bentonite

The accumulation of primary weathering products may also affect the feldspars. Alexander and Hendricks (2) have pointed out that primary weathering products from the feldspars accumulate close to the weathering surface. As Na and K form soluble aluminates it is possible that the aluminum could move some distance before being precipitated in an insoluble form. Ca aluminate is unstable and decomposes in water.

The crystal chemistry relationships of the bases in the feldspars is different than in olivine, augite or hornblende. The bases in the feldspars are held in fairly open channels and are not an integral part of the crystal structure but merely balance the surplus charge (7). If solution of the feldspars is negligible, the decrease in base release could be due to the difficulty of H replacing bases deeper in the crystal lattice. The different feldspars do not vary greatly in the unit cell constants (7). Apparently, replacing the relatively large K ion by smaller Na ions causes the unit cell to collapse slightly. Although the Na ion is smaller than the Ca ion, the higher coordination number of the Ca causes a further distortion and a doubling of the length of the c axis in the Ca feldspars (7). Due to lattice distortion it could be expected that Ca feldspars would be considerably less stable than the Na and K feldspars.

Similarly, Na feldspar may be somewhat less stable than K feldspar. As the ionic radius of H is very small the replacement of any of the bases in the feldspars by H must cause a very great distortion of the crystal. It is doubtful if an H feldspar exists.

Judging from the differences in the rates of release of Ca and Na in labradorite shown in figure 2, and taking into account the Ca:H ratio of 1.3:1, nonetheless Ca is being released faster than Na. A comparison of the graphs in figure 2 for Na and K in albite, microcline and anorthoclase also leads to the conclusion that Ca is being released at a faster rate than either Na or K. Comparison of the rates of release of K and Na in albite, microcline and anorthoclase indicates that K is released faster than Na if molecular ratios are taken into consideration.

Of the micas investigated K was released from muscovite at the fastest rate. As for olivine, augite, hornblende and the feldspars, a rapid initial period of base release from the micas leveled off to a relatively constant rate. This may be attributed in part to the formation of a residual layer of decomposition products around the weathering mineral. Assuming that the release of K from the micas was mainly due to displacement of K by H in the interlattice position, the weathering rate would be decreased as the distance through which the K had to diffuse increased.

Biotite and phlogopite did not differ appreciably in the rates with which their K was replaced. However, the release of Mg from biotite and phlogopite was not similar. For biotite the ratio of Mg:K in the original mineral was about 2:1, but the ratio of Mg:K released during fractionation and treatment with H-bentonite as indicated in table 12, was nearly 1:1. The ratio of the release of Mg:K obtained by electrodialysis of biotite was also approximately 1:1.

If the ratio of Mg:K in the bases released from Mg-bearing micas was similar to the same ratio in the mineral, then decomposition of the mineral would be indicated unless Mg was replaced by some other suitable cation such as Al or Fe. As this was not the case for biotite, K appears to have moved independently of Mg. K is situated between the silica-alumina sheets of the micas and, like the bases of the feldspars, balances a surplus negative charge. However, one K ion may partially balance the charge on both the sheet above and below it. Thus K can form a bonding force holding the silica-alumina layers of mica together. It is conceivable that replacement of K by H would not lead to instability of the mica structure.

Denison and associates (14) observed that during weathering both muscovite and biotite lost K although these minerals retained their crystal structure. Their study

indicated that weathered muscovite in soil was more variable than biotite in K content. They attributed this variation to the formation of secondary muscovite during weathering processes. Barshad (3) has shown that biotite can be converted into vermiculite by prolonged leaching with $MgCl_2$. This shows that although the interlattice ions can be replaced, the basic structure of biotite is relatively stable, a conclusion also arrived at in this study.

From the data in tables 12 and 13 it appears that Mg and K tend to be released from phlogopite in the ratio they were present in the original mineral. As discussed above, the release of Mg from biotite was not equivalent to the release of K. As Mg is present in both phlogopite and biotite in the octahedral layer, the data for the release of bases from phlogopite would indicate that release of K is accompanied by a breakdown of the octahedral layer. Thus biotite and phlogopite seemingly weather differently, although the reason is not apparent. Pauling (43a), in discussing the non-existence of a Mg analogue of kaolinite suggests that an octahedrally coordinated Mg layer would cause the kaolinite-type layer to curve, leading to instability of the structure. Perhaps in the case of phlogopite the K ion increases the stability of the lattice which consists of a brucite layer lying between two silica tetrahedral layers. But when K is removed the basic structure

becomes unstable and Mg is also released.

It is interesting to arrange the minerals studied in order of stability. From the total base release data in table 12 the minerals would be more easily weathered in the following order: olivine > hornblende > augite > muscovite > phlogopite > biotite = labradorite > albite > microcline > anorthoclase. The position of albite is in doubt as Ca was not included in the total bases released. As discussed previously, the release of bases during the fractionation of albite was peculiar. If data from the last release of bases from the H-bentonite coarse clay system shown in table 7 are used as criteria for a stability series the minerals would be more easily weathered in the following order: Olivine > labradorite > muscovite > augite > hornblende > anorthoclase > phlogopite > microcline > albite = biotite. This latter stability series probably more closely approximates the release of bases that could be anticipated from these minerals in soil. While both mechanical disintegration and hydrolysis of minerals probably occur in soils, it is unlikely that the effects would be as pronounced as those attained in the grinding and fractionation processes involved in the investigation of these minerals. On the other hand the minerals were incubated in a more acid medium than is encountered in soils.

In general neither of these two series differs radically from the stability series of Goldich (17) except for the

position of muscovite. Goldich based his stability series on the order of disappearance of minerals during weathering of rocks. The position of muscovite is not unexpected as Denison and associates (14) have shown that muscovite can be identified in the soil even after much of the K has been removed.

Certain inferences pertinent to soils can be made from this investigation. As the rate of release of bases from minerals decreased with particle size, it is important to know the size distribution of the minerals in soils in order to estimate the probable rate of base release. Thus fractionation of soils at small size intervals, particularly of the smaller size classes, should be of value. It is likely that the smallest size fraction containing a certain mineral in appreciable quantities, is responsible for much of the base release in soil from that mineral.

In this study the release of bases from minerals by mechanical disintegration was also appreciable. In soils, freezing and thawing, wetting and drying and other agencies which promote physical disintegration, would also increase the amount of bases released.

This investigation indicated that the degree of Ca or H saturation of the colloidal complex may be important in determining the rate of release of bases from soils. Increasing the Ca saturation of the colloid should have a

marked effect in decreasing base release. Conversely, increasing the H saturation should increase the base release of minerals in soils. This probably explains in part why almost unweathered grains of minerals are commonly found in calcareous soils or in soils with a high degree of Ca saturation. The relationship between saturation of the colloid with bases other than Ca, and base release from minerals was not investigated.

The effect of temperature on base release from muscovite and microcline was found to be appreciable in the temperature range commonly found in soil. The temperature effect was more pronounced on fresh mineral surfaces than on partially weathered surfaces. This may be due to residual weathering products minimizing the effect of temperature on the release of bases from partially weathered surfaces.

The graphs in figures 1 and 2 clearly indicate that as weathering increased the rate of release of bases from all of the minerals studied decreased, regardless of treatment. Thus it is important to know which minerals are present in soils and whether they are in a fresh or a weathered state.

The release of K from the K-bearing feldspars, namely anorthoclase and microcline and from the micas, particularly muscovite, indicated that these could be important sources

of K in soils. The magnitude of the release of K from these minerals would of course depend on the size and state of weathering of the mineral as well as the degree of H saturation of the colloid.

Few specific statements from this study can be made at the present time with regard to Iowa soils. Although some mineralogical data are available for some of the pleistocene soil parent materials (35), no data for primary minerals are available for soil profiles. Some data is available for K release from unfractionated soil profile samples (29)(37a). Several soil series such as the Marshall and Sharpsburg series released high amounts of K while soils like the Seymour series released moderate amounts of K. The Marshall and Sharpsburg series have profiles with slight horizon differentiation whereas the Seymour series has a strongly developed clay accumulation horizon. These series are developed from loess whose origin presumably was the Missouri River bottomlands and apparently had a high content of K-bearing minerals.

Larson (37a) found that a Weller soil released about the same amount of K as a Fayette soil. The Weller series, a forest analogue of Seymour, is more strongly weathered than the Fayette series, also a forest derived soil. The reason for the unexpectedly low release from the Fayette

as compared to the Weller soil may be due to a low K-bearing mineral content of the parent loess. The loess from which the Fayette profile was derived presumably had its origin in the Iowan drift plain. The Weller series and the Sharpsburg and Marshall series were developed from similar loess. Detailed studies on the mineral composition and release studies of fractionated soil profile samples might aid in explaining the differences in the K-release from the Fayette and Weller profiles.

Larson (37a) found that the release of K from the Floyd and Carrington series, soils derived from Iowan drift, was lower than for the Webster soil, a Mankato drift derived soil. Again mineralogical analyses and release studies of fractionated samples may indicate the reason for these differences.

VI SUMMARY AND CONCLUSIONS

A study was undertaken to determine the effect of particle size, degree of Ca and H saturation, temperature and time on the rate of release of bases from bentonite-mineral mixtures. Accordingly, pure mineral specimens of some of the minerals commonly found in soils, were obtained. The minerals that were selected included representatives from each of the principal structural types of silicate minerals and included olivine, augite, hornblende, albite, labradorite, microcline, anorthoclase, muscovite, phlogopite and biotite.

The minerals were pulverized in a ball mill and then fractionated in water by syphoning off the finer fractions at a time calculated from Stokes' Law. The clay fraction was separated at the .2 micron level in a supercentrifuge. The minerals appeared to undergo some mechanical breakdown due to shaking. All the minerals except hornblende dispersed on shaking in water. For hornblende only the silt fraction could be separated from the clay fraction.

The effect of fractionation on the bases in the minerals was investigated by determining the amount of total bases in the coarse clay size of the minerals and the principal bases in the ground but untreated minerals.

The effect of particle size on the release of bases

from minerals was studied by determining the amounts of the principal bases released from three different size fractions incubated with H-bentonite and pure silt size quartz. The ratio of mineral:Bentonite:Quartz was 2:2:3. The mineral-bentonite-quartz mixtures were placed in porous bottomed crucibles and then leached with N. ammonium acetate followed by .05 M. acetic acid in order to resaturate the colloid with H. Similar leachings were repeated at intervals for 239 days. During incubation the samples were stored in a humid atmosphere maintained at approximately 26 degrees C. The ammonium acetate leachates were analyzed for the principal bases contained in them. The acetic acid extracts were not analyzed except for the one following the second incubation period. The acetic acid leachates following the second incubation period were analyzed for the same bases that were determined in the ammonium acetate leachates.

The effect of various degrees of Ca and H saturation was studied by incubating the coarse clay fractions of the minerals with bentonite and quartz in the same ratio as was used in the particle size experiment. The mixtures were first leached with N ammonium acetate succeeded by one of the following acetate solutions: (1).05 M. Ca and .05 M. H (1:1 Ca:H), (2) .1 M. Ca and .05 M. H (2:1 Ca:H), (3) .05 M. Ca (Ca-saturated). The ammonium acetate ex-

tracts were analyzed for the principal bases except Ca. All minerals were included in the 1:1 Ca:H treatment but only augite, albite, microcline, biotite and muscovite were included in the 2:1 Ca:H treatment and the Ca-saturated treatment. Other than the differences in the resaturation leachate, the samples were treated the same as in the particle size experiment, including the use of the same incubation periods between leaching operations. The coarse clay fraction of all of the minerals was incubated with quartz alone in order to appraise the effectiveness of bentonite as a weathering agent. The samples were resaturated with H after the ammonium acetate extractions.

The effect of temperature on base release was observed on the coarse clay fractions of microcline and muscovite. Samples of these minerals were stored in humid atmospheres maintained at 7, 16 and 41 degrees C. The samples were treated with ammonium acetate followed by resaturation with H by .05 M. acetic acid.

The release of bases from the coarse clay fractions of olivine, microcline, muscovite and biotite were electro-dialyzed at a potential of 100 volts for 5 weeks. The solutions were changed weekly and the bases contained in the cathode chamber were determined.

From the above experiments the following conclusions were indicated regarding base release from minerals:

1. The hydrolysis of ground minerals is appreciable but the extent of hydrolysis of bases varies between the different minerals and the different ions in the same mineral.
2. The release of bases from minerals increases with decreasing particle size but the extent to which particle size influences base release varies with different minerals.
3. Increasing the ratio of Ca:H on the colloidal complex decreases the rate of base release.
4. Base release increases with temperature but the effect of increased temperature on base release decreases with time.
5. H-bentonite is an effective weathering agent but its effectiveness varies between minerals.
6. The mechanism by which bases are released from minerals by electrodialysis seems to be governed by the same limitations as release by H- and Ca-bentonite but the rates differ.
7. Fresh minerals release bases at a fast rate but this rate rapidly decreases with time. It appears that the residual primary weathering products retard the release of bases from minerals presumably by accumulating close to the weathering surface.
8. Apparently the release of bases from olivine, augite, hornblende, albite, labradorite, microcline, anorthoclase and phlogopite is accompanied by the breakdown of the crystal lattice in those minerals. Muscovite and biotite do not become unstable when K is released, an opinion of numerous investigators.

9. The ratio of the release of two ions present in the same mineral tends to approximate the ratio in which these ions are present in the unweathered mineral, with increasing time.
10. The silt and coarse clay fractions of the K-bearing minerals studied release bases at appreciable rates. The release of K from unweathered muscovite proceeded at a much faster rate than from phlogopite, biotite and the feldspars. All of these minerals could be important sources of K if present in soils.
11. The order with which the minerals studied release bases approximates Goldichs' (17) stability series with the exception of muscovite.

From the above observations it appears that the rates of release of bases from soils would be affected by the types of minerals present, the size distribution of these minerals, the degree of Ca saturation of the colloid, and to a lesser extent, by the temperature. Due to the lack of mineralogical data for Iowa soils no pertinent observations can be made.

VII. LITERATURE CITED

1. Alexander, L. T. and Byers, H. G. The Hydrolysis of Calcium Feldspar. Amer. Soil Survey Assoc. Report. 16: 21-23. 1936.
2. Alexander, L. t., Hendricks, S. B. and Faust, G. T. Occurrence of Gibbsite in Some Soil Forming Materials. Soil Sci. Soc. Amer. Proc. 6: 52-57. 1941.
3. Barshad, Isaac. Vermiculite and its Relation to Biotite as Revealed by Base Exchange Reactions, X-Ray Analyses, Differential Thermal Curves, and Water Content. Amer. Mineral. 33: 655-678. 1948.
4. Blanck, E. Die Glimmer als Kaliquelle für die Pflanzen und ihre Verwitterung. Jour. Landw. 60:97-110. 1912
5. Bouyoucos, G. J. Rate and Extent of Solubility of Minerals and Rocks under Different Treatments and Conditions. Mich. Agr. Exp. Sta. Tech. Bul. 50. 1921.
6. Bowen, N. L. The Reaction Principle in Petrogenesis. Jour. Geol. 30: 177-198. 1922.
7. Bragg, W. L. Atomic Structures of Minerals. Ithaca, Cornell Univ. Press. 1937.
8. Breazeale, J. F. and Magistad, O. C. Base Exchange in Orthoclase. Arizona Agr. Exp. Sta. Tech. Bul. 24. 1928.
9. Buehrer, T. F. and Williams, J. A. Hydrolysis of Certain Soil Minerals. Soil Sci. Soc. Amer. Proc. 1: 165-170. 1937.
10. Cameron F. K. and Bell, J. M. The Mineral Constituents of the Soil Solution. U. S. Bureau of Soils Bul. 30. 1905.
11. Clarke, F. W. The Data of Geochemistry. U. S. Geol. Survey Bul. 770. 1924.
12. Correns, C. W. and Von Englehardt, W. Neue Untersuchungen über die verwitterung des Kalifeldspates. Chemie der Erde. 12: 1-22. 1938.
13. Dana, E. S. and Ford, W. E. A Textbook of Mineralogy. 4th ed. N. Y., John Wiley and Sons Inc. 1932.

14. Denison, I. A., Fry, W. H. and Gile, P. L. Alteration of Muscovite and Biotite in the Soil. U. S. D. A. Tech. Bul. 128. 1929.
15. De Turk, E. Potassium Bearing Minerals as a Source of Potassium for Plant Growth. Soil Sci. 8:269-301. 1919.
16. Drosdoff, M. and Nearpass, D. C. Quantitative Microdetermination of Magnesium in Plant Tissue and Soil Extracts. Anal. Chem. 20: 673-674. 1948.
17. Goldich, Samuel S. A Study in Rock-Weathering. Jour. Geol. 46: 17-58. 1938.
18. Graham, E. R. Primary Minerals of the Silt Fraction as Contributors to the Exchangeable-Base Level of Acid Soils. Soil Sci. 49: 277-281. 1940.
19. Graham, E. R. Colloidal Organic Acids as Factors in the Weathering of Anorthite. Soil Sci. 52: 291-296. 1941.
20. Graham, E. R. Soil Development and Plant Nutrition. Mineralogical and Chemical Composition of Sand and Silt Separates in Relation to the Growth and Chemical Composition of Soybeans. Soil Sci. 55: 263-273. 1943.
21. Grim, R. E. Modern Concepts of Clay Minerals. Jour. Geol. 50: 225-275. 1942.
22. Hall, N. S. A Laboratory Method for the Artificial Alteration of Aluminosilicates. North Carolina Agr. Exp. Sta. Tech. Bul. 77. 1943.
23. Hardy, F. and Rodrigues, G. Soil Genesis from Andesite in Granada, British West Indies. Soil Sci. 48: 361-384. 1939.
24. Hardy, F. and Rodrigues, G. The Genesis of Davidson Clay Loam. Soil Sci. 48: 483-495. 1939.
25. Harrison, J. B. Katamorphism of Igneous Rocks Under Humid Tropical Conditions. Harpenden, Imp. Bur. Soil Sci. 1-79. 1933.
26. Hendricks, S. B. and Jefferson, M. E. Polymorphism of the Micas with Optical Measurements. Amer. Mineral. 24: 729-771. 1939.

27. Humbert, R. P. and Marshall, C. E. Mineralogical and Chemical Studies of Soil Formation from Acid and Basic Igneous Rocks in Missouri. Missouri Agr. Exp. Sta. Research Bul. 359. 1943.
28. Humfeld, H. and Alben, A. C. Electrodialysis of the Soil. I. A Study of the Method. Jour. Amer. Soc. Agron. 19: 984-993. 1927.
29. Hutton, C. E. Studies of Loess-Derived Soils of Southwestern Iowa. Soil Sci. Soc. Amer., Proc. 12: 424-431. 1947.
30. Jackson, M. L. and Truog, E. Influence of Grinding Soil Minerals to Near Molecular Size on their Solubility and Base Exchange Properties. Soil Sci. Soc. Amer. Proc. 4: 136-143. 1939.
31. Jackson, M. L., Tyler, S. A., Willis, A.L., Bourbeau, G. C. and Pennington, R. P. Weathering Sequence of Clay Size Minerals in Soils and Sediments. I. Jour. of Phys. and Colloid Chem. 52: 1237-60. 1948.
32. Jeffries, C. D. The Use of the X-Ray Spectrometer in the Determination of the Essential Minerals in Soils. Soil Sci. Soc. Amer. Proc. 12: 135-140. 1947.
33. Jeffries, C. D. and White, J. W. Some Mineralogical and Chemical Characteristics of a Hagerstown Soil Profile. Soil Sci. Soc. Amer. Proc. 2: 133-141. 1937.
34. Jeffries, C. D. and White, J. W. Variations in the Composition of Feldspar from a Hagerstown Soil Profile. Soil Sci. Soc. Amer. Proc. 3: 26-31. 1938.
35. Kay, G. F. and Graham, J. B. The Illinoian and Post-Illinoian Pleistocene Geology of Iowa. Iowa Geol. Survey. 38: 1-262. 1941.
36. Kelley, W. P. Modern Clay Researches in Relation to Agriculture. Jour. Geol. 50: 307-319. 1943.
37. Kelley, W. P. and Jenny, Hans. The Relation of Crystal Structure to Base Exchange and its Bearing in Base Exchange in Soils. Soil Sci. 41: 367-382. 1936.
- 37a. Larson, W. E. Release of Na from Nonreplaceable to Replaceable Forms in Iowa Soils and the Response of Various Crops to Na Fertilization. Unpublished Ph.D. Thesis. Ames, Iowa, Iowa State College Library. 1949.

38. Lawton, K. The Determination of Exchangeable Potassium in Soils Using Hexanitradiphenylamine. Soil Sci. Soc. Amer. Proc. 10: 126-128. 1945.
39. Leith, C. K. and Mead, W. J. Metamorphic Geology. N. Y., Henry Holt and Co. 1915.
40. Marshall, C. E. and Jeffries, C. D. Mineralogical Methods in Soil Research: Part 1. The Correlation of Soil Types and Parent Materials, with Supplementary Information on Weathering Processes. Soil Sci. Amer. Proc. 10: 397-405. 1945.
41. Mattson, Sante. Electrodialysis of the Colloidal Soil Material and the Exchangeable Bases. Jour. Agr. Res. 33: 553-567. 1926.
42. Mikkelsen, D. S., Toth, S. J. and Prince, A. L. Determination of Magnesium by Thiazol Yellow Method. Soil Sci. 66: 385-92. 1948.
43. Morey, G. W. and Ingerson, Earl. The Pneumatolytic and Hydrothermal Alteration and Synthesis of Silicates. Econ. Geol. 32: 607-761. 1937.
- 43a. Pauling, L. The Structure of the Chlorites. Nat. Acad. Sciences Proc. 16: 578-582. 1930.
44. Peech, M. Dean, L. A. and Reed, J. F. Methods of Soil Analysis for Soil Fertility Investigations. U. S. D. A. Circular 757. 1947.
45. Pettijohn, F. J. Persistence of Heavy Minerals and Geologic Age. Jour. Geol. 49: 610-625. 1941.
46. Reiche, Parry. A Survey of Weathering Processes of Products. Albuquerque, Univ. of New Mexico Press. 1945.
47. Reitemeier, R. F., Holmes, R. S., Brown, I. C., Klipp, Lorraine, W., Parks, R. C. Release of Non-exchangeable K by Greenhouse, Neubauer and Laboratory Methods. Soil Sci. Soc. Amer. Proc. 12: 158-162. 1947.
48. Riecken, F. F., Allaway, W. H. and Smith, Guy D. Some Soil Classification and Mapping Problems in the Wisconsin Drift Area of Iowa. Soil Sci. Soc. Amer. Proc. 12: 432-440. 1947.

- 48a. Ross, C. S. and Hendricks, S. B. Minerals of the Montmorillonite Group, Their Origin and Relation to Soils and Clays. Geol. Survey Prof. Paper 205-B. 1945.
49. Smithson, F. The Alteration of Detrital Minerals in the Mesozoic Rocks of Yorkshire. Geol. Mag. 78: 97-112. 1941.
50. Steidtmann, Edward. A Graphic Comparison of the Alteration of Rocks by Weathering with their Alteration by Hot Solutions. Econ. Geol. 3: 381-409. 1908.
51. Stevens, R. E. Hydrogen Ion Concentrations Caused by the Solution of Silicate Minerals. Jour. Wash. Acad. Sciences. 22: 540-547. 1932.
52. Stevens, R. E. Studies on the Alkalinity of Some Silicate Minerals. U. S. Geol. Survey Prof. Paper. 185-A. 1934.
53. Stout, P. R. Univ. of Calif. Preparation of H-Bentonite by means of Exchange Resins. (Private Communication). 1948.
54. Tamm, Olof. Experimental Study of the Weathering of Silicate Minerals. Arkiv Kemi Mineral. Geol. 11A, No. 17, 27pp. (1934). Original not available for examination; abstracted in Chem. Abstracts 28: 6396. 1934.
55. Vandecaveye, S. G. The Liberation of K from Feldspars, and of K and CO₂ from Soils by Fertilizer and Acid Treatments. Soil Sci. 16: 389-406. 1923.
56. Van Hise, C. R. A Treatise on Metamorphism. U. S. Geol. Surv. Monog. 47. 1904.
57. Volk, Garth, W. Optical and Chemical Studies of Muscovite. Amer. Mineral 24: 255-266. 1939.
58. Volk, N. J. Formation of Muscovite in Soils and Refinements in Specific Gravity Separations. Amer. Jour. of Sci. (5) 26: 114-129. 1933.
59. Willard, H. H. and Diehl, H. Advanced Quantitative Analysis. N. Y., D. Van Nostrand Co. Inc. 1943.

60. Willard, H. H. and Furman, N. H. Elementary Quantitative Analysis. (3rd ed.) N. Y., D. Van Nostrand Co. Inc. 1940.
61. Winchell, A. N. Studies in the Mica Group. Amer. Jour. Sci. (5) 9: 309-327. 1925.

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